

## Reactions of *cis*- and *trans*-Bromo(dimethylformamide) and Bis(dimethylformamide)bis(ethylenediamine)chromium(III) in Dimethylformamide. Kinetics, Stereochemistry, and Equilibria

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*trans*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> isomerizes to *cis*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> (87 ± 2%, 40°; 81 ± 2%, 67°) and solvolyzes with ethylenediamine loss to give Cr(en)(DMF)<sub>4</sub><sup>3+</sup> (13 ± 2%, 40°; 19 ± 2%, 67°). There is no accumulation of unidentate en complex. Similarly, *trans*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup> directly gives two products: *cis*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup> (33 ± 3%, 48°; 40 ± 3%, 67°) and *cis*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> (67 ± 3%, 48°; 60 ± 3%, 67°). For the latter reaction it is shown that solvolysis does not proceed via *trans*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup>. The complete change in configuration in bromide solvolysis contrasts with the strict retention observed in mercuric and silver ion promoted solvolysis. Significant net loss of ethylenediamine is not observed accompanying this reaction except in the presence of added bromide ion. Rate and stereochemical data and activation parameters are reported for these reactions. The interconversion of *cis*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup> and *cis*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup>(+Br<sup>-</sup>) has been investigated over a range of bromide ion concentration and temperature. Activation parameters are recorded. These reactions proceed with complete retention of geometric configuration under all conditions. The anation rate data show a typical bromide dependence where multiple ion associated complexes are involved. An I<sub>a</sub> mechanism has been assigned to both reactions. The equilibria in DMF are dominated by the *cis*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> and *cis*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup> species except at zero bromide where some (10%) *trans*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> is found. The results are shown to be consistent with the trends previously established in similar Cr(III) and Co(III) systems. In the absence of bromide, the thermodynamic stability of the Cr(en)<sub>2</sub> moiety with respect to ethylenediamine loss in DMF has been determined. These results are discussed in relation to the potential importance of amine cleavage paths in all the substitution reactions studied. Comparisons are made with the recently studied analogous dimethyl sulfoxide (DMSO) system.

### Introduction

The first stage of bromide ion solvolysis for the *cis*- and *trans*-dibromobis(ethylenediamine)chromium(III) complexes in DMF was reported recently.<sup>1</sup> The bromochlorochromium(III) complexes were also investigated in DMF as well as in DMSO.<sup>1</sup> Comparisons were made between the then complete dibromo-, dichloro-, and bromochlorocobalt(III) and -chromium(III) systems in the two solvents DMF and DMSO. In this paper we consider the second stages of reaction for the dibromochromium(III) complexes in DMF. This research completes this particular system in that the reactions of the complete range of complexes have now been studied, namely, the dibromo, bromo(dimethylformamide), and bis(dimethylformamide) *cis*-*trans* isomeric pairs. We also report the synthesis of the new mono(ethylenediamine)chromium(III) complexes [Cr(en)(DMSO)<sub>4</sub>](ClO<sub>4</sub>)<sub>3</sub> and [Cr(en)(DMF)<sub>4</sub>](ClO<sub>4</sub>)<sub>3</sub>.

We recently reported the isolation of the elusive trans-solvento complexes<sup>2</sup> in the Cr(III) systems. Thus Watts and Palmer have investigated the complete dibromo-DMSO system<sup>3</sup> analogous to the work considered here and have reexamined<sup>4</sup> their initial findings for the dichloro complexes in DMSO<sup>5</sup> to include the reactions of the new *trans*-chloro(dimethyl sulfoxide) and *trans*-bis(dimethyl sulfoxide) cations which were not observed in their original study.<sup>5</sup> We have also studied these reactions as well as their DMF analogs<sup>7</sup> in the dichloro system,<sup>5,6</sup> and the relevant results are considered here for comparison.

### Experimental Section

**Preparation of Complexes.** The known<sup>1,2</sup> complexes *cis*- and *trans*-[Cr(en)<sub>2</sub>(DMF)Br](ClO<sub>4</sub>)<sub>2</sub>, *trans*-[Cr(en)<sub>2</sub>(DMF)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub>,<sup>8</sup> and *cis*-[Cr(en)<sub>2</sub>(DMF)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> and *cis*-[Cr(en)<sub>2</sub>(DMF)<sub>2</sub>](NO<sub>3</sub>)(ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O were freshly prepared and analyzed satisfactorily. Typical analyses have been given.<sup>1,2</sup>

**Tetrakis(dimethyl sulfoxide)mono(ethylenediamine)chromium(III) Triperchlorate, [Cr(en)(DMSO)<sub>4</sub>](ClO<sub>4</sub>)<sub>3</sub>.** [Cr(en)(OH<sub>2</sub>)(O<sub>2</sub>)<sub>2</sub>·H<sub>2</sub>O]<sup>9</sup> was carefully rendered free of excess dichromate by allowing the complex to form in the cold as in the original synthesis<sup>9,10</sup> and then through successive cold aqueous extractions of the sparingly soluble reaction product. The highly crystalline olive green complex was used

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immediately.<sup>9,10</sup> This material was added in small portions to perchloric acid (5 M, 0°) with stirring until the pH was 1. It is important that complex is added to the acid, not *vice versa*. A concentrated solution of the deep red Cr(en)(OH<sub>2</sub>)<sub>4</sub><sup>3+</sup> in 0.1 M HClO<sub>4</sub> so obtained was warmed to complete the reaction. The clear solution was then cooled, diluted with a tenfold volume of DMSO, and heated on a steam bath for 1 hr during which time the mixture became a deep violet. The resultant solution of Cr(en)(DMSO)<sub>4</sub><sup>3+</sup> was cooled and then filtered slowly into a 50-fold volume excess of ethanol from which crystals separated. The collected product was washed with ethanol and ether and then dissolved in pure DMSO and refluxed (30 min) to ensure complete DMSO substitution of the aquo ligands. The product, again crystallized with ethanol, was finally recrystallized twice from water (0°) or DMSO by the slow addition of aqueous sodium perchlorate. Violet needles were obtained in 60% yield (based on peroxo complex). *Anal.* Calcd for [Cr(en)(DMSO)<sub>4</sub>](ClO<sub>4</sub>)<sub>3</sub>: C, 16.6; H, 4.5; N, 3.9; S, 17.8; Cl, 14.7. Found: C, 16.3; H, 4.5; N, 4.0; S, 17.7; Cl, 14.6.

**Caution!** Peroxides and perchlorates are potentially explosive. Also, care should be exercised in mixing DMSO and perchloric acid solutions.

**Tetrakis(dimethylformamide)mono(ethylenediamine)chromium(III) Triperchlorate, [Cr(en)(DMF)<sub>4</sub>](ClO<sub>4</sub>)<sub>3</sub>.** **Method 1.** A procedure similar to that given immediately above was followed. Cr(en)(OH<sub>2</sub>)<sub>4</sub><sup>3+</sup> in 0.1 M HClO<sub>4</sub> was diluted with DMF and heated (1 hr) to yield pink Cr(en)(DMF)<sub>4</sub><sup>3+</sup>. The product was crystallized with ethanol and again heated in DMF (reflux, 30 min). Recrystallization from water (0°) or DMF by the addition of cold aqueous NaClO<sub>4</sub> gave pure [Cr(en)(DMF)<sub>4</sub>](ClO<sub>4</sub>)<sub>3</sub> as pink needles in about 50% yield. There is more decomposition in this preparation than in the analogous DMSO synthesis.

**Method 2.** [Cr(en)(DMSO)<sub>4</sub>](ClO<sub>4</sub>)<sub>3</sub> was heated in DMF for 2 hr on a steam bath. The violet solution slowly became pink over this period. The product was precipitated in excess ethanol; the pure complex was isolated as described in method 1. The yield was 90% (or about 55% based on peroxo complex). This product had an absorption spectrum identical with that prepared by the first method; the absence of DMSO in the product was confirmed by ir measurements and microanalysis for S (nil). *Anal.* Calcd for [Cr(en)(DMF)<sub>4</sub>](ClO<sub>4</sub>)<sub>3</sub>: C, 23.3; H, 5.2; N, 12.0; Cl, 15.1. Found: C, 23.2; H, 5.1; N, 11.7; Cl, 15.0.

**Characterization.** Known compounds were characterized as previously described<sup>2</sup> and were always recrystallized to a constant absorption spectrum (ε, ±1%). The purity of the new complexes [Cr(en)(DMSO)<sub>4</sub>](ClO<sub>4</sub>)<sub>3</sub> and [Cr(en)(DMF)<sub>4</sub>](ClO<sub>4</sub>)<sub>3</sub> was established similarly. It should be noted that the absorption spectra

Table I. Observed and Calculated Isosbestic Points for the Reaction

$$cis-Cr(en)_2(DMF)Br^{2+} \xrightleftharpoons{DMF} cis-Cr(en)_2(DMF)_2^{3+} + Br^-$$

Starting complex	$\lambda, \epsilon$ (nm, $M^{-1} \text{ cm}^{-1}$ )	
	Obsd <sup>a</sup>	Calcd
<i>cis</i> -Cr(en) <sub>2</sub> (DMF) <sub>2</sub> <sup>3+</sup>	384.5, 71.0	
	433, 32.6	
	518, 92.9	
<i>cis</i> -Cr(en) <sub>2</sub> (DMF)Br <sup>2+</sup>	384, 70.2	383, 70.7
	433.5, 32.8	431, 32.4
	516, 94.0	517, 93.8
<i>cis</i> -Cr(en) <sub>2</sub> Br <sub>2</sub> <sup>+</sup> <sup>b</sup>	383, 70.5	
	434, 33.0	
	517, 95.0	

<sup>a</sup> Arbitrary temperature (40°);  $[Br^-]_0 = 0$ . <sup>b</sup> Isosbestic points become clear only after approximately  $5t_{1/2}$  of primary solvolysis.

of these tetrakis(solvento) complexes are quite different; thus the presence of any (DMSO)<sub>4</sub> complex ( $\geq 2\%$ ) in  $[Cr(en)(DMF)_4](ClO_4)_3$  is readily detected (see synthetic method 2). Infrared measurements established that complexed solvent was oxygen bonded<sup>2</sup> ( $[Cr(en)(DMSO)_4](ClO_4)_3$ ,  $\nu(S=O)$  990  $\text{cm}^{-1}$  (s);  $[Cr(en)(DMF)_4](ClO_4)_3$ ,  $\nu(C=O)$  1650  $\text{cm}^{-1}$  (vs); KBr disks). Microanalyses (C, H, N, S, Cl) were performed by the Australian Microanalytical Service, CSIRO, Melbourne.

**Solvents, Other Materials, and Instrumentation.** Details of DMF and  $N(C_2H_5)_4Br$  purification have been given.<sup>1</sup> The instruments used were those employed previously.<sup>2,11</sup> Other chemicals were reagent grade.

**Kinetic Techniques.** All reactions were studied spectrophotometrically on perchlorate salts by the methods outlined previously.<sup>1,11,12</sup> Some runs were more conveniently performed by standard sampling techniques but most were carried out directly in the spectrophotometer cell which was housed in the thermostatically controlled cell block. Temperature control ( $\pm 0.05$  to  $\pm 0.15^\circ$  in the 30–70° range) was maintained through a Haake thermostat and pump in an external water bath. Equilibrium measurements were made on presampled solutions which were allowed to react for at least  $6t_{1/2}$  in an oil bath controlled to  $\pm 0.02^\circ$  with a mercury-toluene regulator. We followed the routine precautions of excluding light and performing operations with anhydrous DMF solutions under dry nitrogen.

## Results

The complete dibromo-DMF system showing only the observed reaction paths is shown schematically in Figure 1. The pseudo-first-order rate constant for the conversion of complex 1 to complex 2 is labeled  $k_{12}$ , and similarly for the other paths shown.<sup>3</sup> The primary solvolyses  $1 \rightarrow 2$  and  $4 \rightarrow 5$  have been considered previously<sup>1</sup> and we now turn to the other reactions.

**I. *cis*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup>  $\rightleftharpoons$  *cis*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> + Br<sup>-</sup>. Stereochemistry.** Changes in absorption spectra with time which characterize this reversible reaction are shown in Figure 2. The set of sharp isosbestic points (Table I) is independent of starting complex—1 (after  $5t_{1/2}$  of reaction  $1 \rightarrow 2$ ), 2, or 3—in the bromide ion range  $6.5 \times 10^{-3}$  to  $6.5 \times 10^{-2} M$  and is not temperature dependent (25–60°). At very low  $[Br^-]_0$ , the isomerization  $3 \rightarrow 6$  interferes and under these conditions sharp isosbestic points are not observed. However, under all other conditions, the light absorption could be accurately accounted for in terms of only the *cis* complexes 2 and 3 (see Figure 4 for the component absorption spectra). Thus, solvolysis of *cis*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup> and bromide anation of *cis*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> proceed with complete retention of configuration (Table I).

**Kinetics.** Commencing with the *cis*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup> complex,  $k_0 (=k_{23} + k_{32})$  was calculated by treating the reaction as a simple reversible first-order process,  $A \rightleftharpoons B$ . Absorbance data ( $D, t$ ) were treated by one of three standard methods: (i) the Guggenheim approach,<sup>13</sup> (ii) direct measurement of  $D_\infty$  and then plotting  $\ln |D - D_\infty|$  against  $t$ , or (iii) nonlinear least-squares fitting<sup>14</sup> to the expression  $D = D_\infty +$

Table II. Pseudo-First-Order Rate Constants for the Reactions

$$cis-Cr(en)_2(DMF)Br^{2+} \xrightleftharpoons[k_{32}]{k_{23}} cis-Cr(en)_2(DMF)_2^{3+} + Br^-$$

$T, ^\circ C$	$10^3$		$10^5$		$10^5$	
	$[Complex]_0, ^a$ $M$	$[N(C_2H_5)_4Br]_0, ^a$ $M$	$[Br^-]_0, ^c$ $M$	$(k_{23} + k_{32}), ^b$ $\text{sec}^{-1}$	$k_{23}, ^d$ $\text{sec}^{-1}$	$k_{32}, ^e$ $\text{sec}^{-1}$
40.2	8.38	0	8.38	12.8	6.3	6.5
40.2	8.66	8.58	16.7	15.8	5.7	10.1
40.2	8.62	18.9	27.5	16.8	5.2	11.6
40.25	8.29	27.6	35.9	16.9	5.2	11.7
60.50	5.52	0	5.52		37.0 <sup>f</sup>	
60.90	7.57	0	7.57		36.8 <sup>f</sup>	
60.95	8.53	0	8.53	138.8	50.0	88.8
61.3	7.52	15.4	22.9	223.0	44.7	178.3

<sup>a</sup> *cis*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup> reactant only. <sup>b</sup> Obtained by conventional  $A \rightleftharpoons B$  treatment;  $\pm 2\%$ . <sup>c</sup> Total bromide. <sup>d</sup>  $\pm 10\%$ . <sup>e</sup>  $\pm 5\%$ . <sup>f</sup> Calculated from the zero-time limiting slope of curved first-order kinetics plots for an  $A \rightarrow B$  reaction;  $\pm 20\%$ .

Table III. Pseudo-First-Order Rate Constants for the Reactions

$$cis-Cr(en)_2(DMF)_2^{3+} + Br^- \xrightleftharpoons[k_{23}]{k_{32}} cis-Cr(en)_2(DMF)Br^{2+}$$

$T, ^\circ C$	$10^3$		$10^5$		$10^5$	
	$[complex]_0, ^a$ $M$	$[Br^-]_0, ^b$ $M$	$(k_{23} + k_{32}), ^c$ $\text{sec}^{-1}$	$10^5 k_{23}, ^d$ $\text{sec}^{-1}$	$10^5 k_{32}, ^e$ $\text{sec}^{-1}$	
40.0	6.47	3.46	4.50 <sup>f</sup>	3.3 <sup>f</sup>	1.20 <sup>f</sup>	
39.95	6.49	6.49	7.90	5.0	2.90	
40.0	6.49	6.92	11.2			
40.0	6.51	10.4	13.7			
40.0	6.49	13.0	14.5	4.2	10.3	
40.05	6.49	16.3	16.7	4.5	12.2	
40.1	6.49	22.8	17.2	5.3	11.9	
40.0	6.49	32.5	17.7	5.7	12.0	
40.0	6.58	33.4	17.2	5.2	12.0	
40.05	6.49	64.9	16.5	4.5	12.0	
60.85	7.57	23.5	193.3	39.2	154.1	
60.95	12.45	8.51	97.0 <sup>f</sup>	52.5 <sup>f</sup>	44.5 <sup>f</sup>	
60.95	8.51	8.51	128.0	48.8	79.2	

<sup>a</sup> All data obtained with *cis*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup>. <sup>b</sup>  $[N(C_2H_5)_4Br]_0 = [Br^-]_0 =$  total bromide. <sup>c</sup> Conventional  $A \rightleftharpoons B$  treatment;  $\pm 2\%$ . <sup>d</sup>  $\pm 10\%$ . <sup>e</sup>  $\pm 5\%$ . <sup>f</sup> Some side reaction experienced under these conditions (see text).

$(D_0 - D_\infty)e^{-k_0 t}$  where both  $k_0$  and  $D_\infty$  could be used as parameters. The results of each method were equivalent. The logarithmic rate plots were remarkably linear for at least  $4t_{1/2}$  under all conditions studied despite the simplifying assumption of an  $A \rightleftharpoons B$  process. It will be seen ahead that  $k_{32}$  is significantly bromide dependent; the other component ( $k_{23}$ ) of  $k_0$  is essentially bromide independent. It therefore appears that no marked change occurs in the proportions of the various ion aggregates of the *cis*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> species during reaction. The measured or computed  $D_\infty$  value directly yields the equilibrium ratio of the two *cis* complexes ( $k_{23}/k_{32}$ ) and hence the individual constants  $k_{23}$  and  $k_{32}$  were readily evaluated from  $k_0$ . Note that although  $k_{23}$  can be directly measured by assuming an  $A \rightarrow B$  process and thereby neglecting reversibility, extrapolation of the necessarily curved conventional first-order rate plot to  $t = 0$  was too imprecise to be useful. Results are collected in Table II.

Similar calculations were made on data derived from *cis*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> reactant; these results are given in Table III. The results of Tables II and III for the same reaction are not directly comparable since a different  $[complex]_0$  was used in each case; however, within experimental error, values of  $k_0$  and  $k_{32}$  which are independent of  $[complex]_0$  at high  $[Br^-]_0$  and  $k_{23}$  which is independent of  $[complex]_0$  over the complete bromide range are the same for the two sets of data

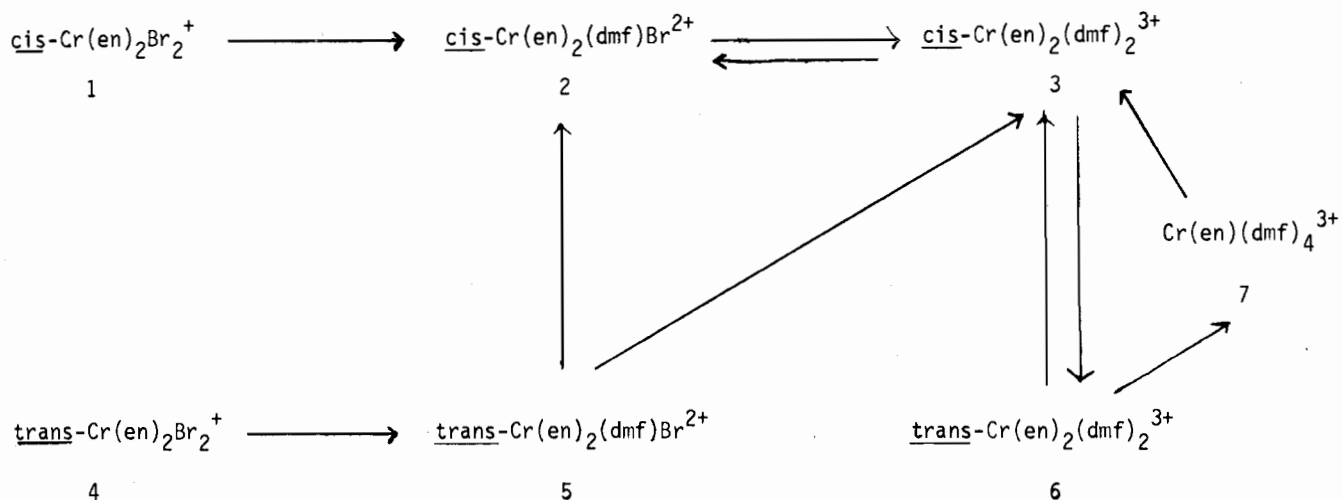


Figure 1. The dibromo-DMF system.

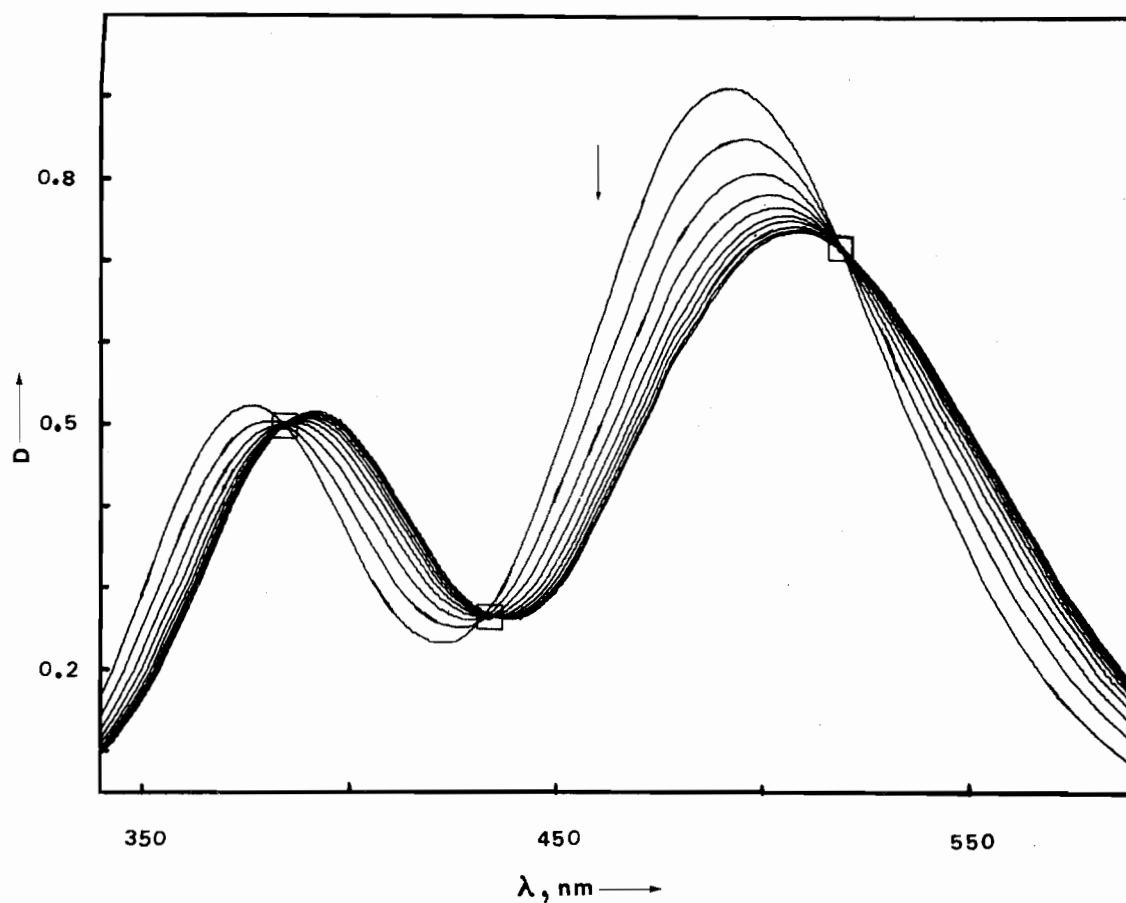
Figure 2. Changes in absorption spectra for the bromide anation of  $\text{cis-Cr(en)}_2(\text{DMF})_2^{3+}$  in DMF.

Table IV. Activation Parameters for the Reactions

Rate constant	$\text{cis-Cr(en)}_2(\text{DMF})\text{Br}^{2+} \xrightleftharpoons[k_{32}]{k_{23}} \text{cis-Cr(en)}_2(\text{DMF})_2^{3+} + \text{Br}^-$				
	$10^5 k$ (50°), sec <sup>-1</sup>	$\Delta G^\ddagger$ (50°), kcal mol <sup>-1</sup>	$E_a^c$ , kcal mol <sup>-1</sup>	$\Delta H^\ddagger,^c$ kcal mol <sup>-1</sup>	$\Delta S^\ddagger$ , cal mol <sup>-1</sup> deg <sup>-1</sup>
$k_{23}^a$	16.2	24.7	23.5	22.9	-5.5
$k_{23} + k_{32}^b$	60.7	23.7	24.0	23.4	-1.0

<sup>a</sup>  $[\text{N}(\text{C}_2\text{H}_5)_4\text{Br}]_0 = 0$ . <sup>b</sup>  $[\text{N}(\text{C}_2\text{H}_5)_4\text{Br}]_0$  in excess. <sup>c</sup>  $\pm 1.0$  kcal mol<sup>-1</sup>.

(Tables II and III). The random scatter about the mean value of  $k_{23}$  is partly an artifact arising out of sectioning  $k_0 (=k_{23} + k_{32})$  into the smaller  $k_{23}$  and larger  $k_{32}$  and the error introduced is greater at lower  $[\text{Br}^-]_0$ ;  $k_{23}$  shows no systematic bromide dependence.

Values for  $k_0$  were also obtained by indirectly studying the reaction following the primary  $\text{cis-Cr(en)}_2\text{Br}_2^+$  solvolysis in DMF<sup>1</sup> (reaction 1  $\rightarrow$  2, Figure 1). The application of standard consecutive first-order reaction treatments<sup>15</sup> to the absorbance data yielded values for  $k_0$  (and  $k_{23}$ ,  $k_{32}$ ) in reasonable ( $\pm 5\%$ ) agreement with those obtained by more direct measurement.

Activation parameters calculated graphically are recorded

Table V. Stereochemistry of the Reaction

$$\text{trans-Cr(en)}_2(\text{DMF})\text{Br}^{2+} \begin{cases} \xrightarrow{k_{52}} \text{cis-Cr(en)}_2(\text{DMF})\text{Br}^{2+} \\ \xrightarrow{k_{53}} \text{cis-Cr(en)}_2(\text{DMF})_2^{3+} + \text{Br}^- \end{cases}$$

$T, ^\circ\text{C}$	Isosbestic points $\lambda, \epsilon$ (nm, $M^{-1} \text{cm}^{-1}$ )		$R^f$	% <i>cis</i> -Cr(en) <sub>2</sub> (DMF)Br <sup>2+</sup> in products <sup>g</sup>
	Obsd <sup>b</sup>	Calcd <sup>c</sup>		
48.4	553, 40.3 <sup>d</sup>	553, 40.2	0.50	33
	427, 30.7 <sup>d</sup>	426, 31.1		
67.2	555, 40.7 <sup>e</sup>	555, 40.4	0.67	40
	426, 31.1 <sup>e</sup>	427, 31.0		

<sup>a</sup> Two temperature extremes examined. <sup>b</sup>  $[\text{N}(\text{C}_2\text{H}_5)_4\text{Br}]_0 = 0$ . <sup>c</sup> Isosbestic points calculated from average product ratio ( $R$ ). <sup>d</sup> Calculated 35 and 30% *cis*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup>, respectively, for each isosbestic point (553 and 427 nm). <sup>e</sup> Calculated 42 and 38% *cis*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup>, respectively (555 and 426 nm). <sup>f</sup>  $R = k_{52}/k_{53}$ . <sup>g</sup>  $10^2 R/(1 + R); \pm 3\%$ .

Table VI. First-Order Rate Constants for the Reaction

$$\text{trans-Cr(en)}_2(\text{DMF})\text{Br}^{2+} \begin{cases} \xrightarrow{k_{52}} \text{cis-Cr(en)}_2(\text{DMF})\text{Br}^{2+} \\ \xrightarrow{k_{53}} \text{cis-Cr(en)}_2(\text{DMF})_2^{3+} + \text{Br}^- \end{cases}$$

$T, ^\circ\text{C}$	Isosbestic points $\lambda, \epsilon$ (nm, $M^{-1} \text{cm}^{-1}$ )			
	Obsd <sup>b</sup>	Calcd <sup>c</sup>	$R^f$	% <i>cis</i> -Cr(en) <sub>2</sub> (DMF) <sub>2</sub> <sup>3+</sup> in products <sup>g</sup>
66.6	554, 32.7	554, 32.7	4.25	81
40.1	424.5, 29.0	424.5, 29.2	6.7	87
	547, 38.4	547, 38.4		
25.0 <sup>d</sup>	422, 28.0	422, 28.4		100
	544, 40.0	543, 40.6		
	414, 26.6	414, 26.0 <sup>e</sup>		
	430, 31.0	430, 30.7 <sup>e</sup>		

<sup>a</sup>  $[\text{Br}^-]_0 = 0$ . <sup>b</sup>  $\pm 10\%$ . <sup>c</sup>  $\pm 15\%$ . <sup>d</sup> Catalyzed.

in Table IV.

**II. *trans*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup> → *cis*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup> and *cis*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> + Br<sup>-</sup>.** The following results refer only to reaction in the absence of added bromide ion.

**Stereochemistry.** Sharp isosbestic points (Figure 3) were observed at all temperatures for at least  $1t_{1/2}$  of *trans*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup> consumption in DMF, suggesting one or more products formed in constant proportions. Indeed, calculations at each of the isosbestic points (Table V) yielded internally consistent results based on the assumption that *cis*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup> and *cis*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> were the products. The proportion of these two products is kinetically controlled (see Discussion). Complete spectral analysis [three wavelengths were used (see ref 12)] of the reacting system for the three light-absorbing species (Figure 4) confirmed the constant product proportions recorded in Table V. There was no evidence for loss of ethylenediamine.

**Kinetics.** The observed first-order rate constant  $k_0 (=k_{52} + k_{53})$  was evaluated from plots of  $\ln |D - D_\infty|$  against  $t$ , where  $D_\infty$  represents the absorbance of the constant product mixture assuming complete conversion.  $D_\infty$  was calculated using the known product ratio, except for plots made at a convenient *cis*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup>-*cis*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> isosbestic point (517 nm) where a knowledge of the product proportions is redundant.  $k_{52}$  and  $k_{53}$  were calculated from  $k_0$  and the known product ratio ( $k_{52}/k_{53}$ ). Results are shown in Table VI. Although values for  $k_0$  calculated at several wavelengths for any one run were in excellent agreement ( $\pm 2\%$ ), confirming the assigned steric course of reaction, the reproducibility (several runs) was not good ( $\pm 10\%$ ). This difficulty arose from an uncharacterized catalytic reaction (*vide infra*) which in many cases limited spectral measurements to  $0.5t_{1/2}$  but more usually  $1t_{1/2}$ . Thus, although the stereochemistry was re-

Table VII. Activation Parameters for the Reactions

$$\text{trans-Cr(en)}_2(\text{DMF})\text{Br}^{2+} \begin{cases} \xrightarrow{k_{52}} \text{cis-Cr(en)}_2(\text{DMF})\text{Br}^{2+} \\ \xrightarrow{k_{53}} \text{cis-Cr(en)}_2(\text{DMF})_2^{3+} + \text{Br}^- \end{cases}$$

Rate constants <sup>a,b</sup>	$10^5 k$ (50°), sec <sup>-1</sup>	$\Delta G^\ddagger$ (50°), kcal mol <sup>-1</sup>	$E_a, ^c$ kcal mol <sup>-1</sup>	$\Delta H^\ddagger, ^c$ kcal mol <sup>-1</sup>	$\Delta S^\ddagger, \text{ cal}$ mol <sup>-1</sup> deg <sup>-1</sup>
$k_0$	3.45	25.6	25.2	24.5	-3.5
$k_{52}$	1.2	26.3	28.0	27.4	+3.5
$k_{53}$	2.25	25.8	23.7	23.0	-8.5

<sup>a</sup>  $k_0 = k_{52} + k_{53}$ . <sup>b</sup>  $[\text{Br}^-]_0 = 0$ . <sup>c</sup>  $\pm 1.0$  kcal mol<sup>-1</sup> ( $k_0$ );  $\pm 1.5$  kcal mol<sup>-1</sup> ( $k_{53}$ );  $\pm 2.0$  kcal mol<sup>-1</sup> ( $k_{52}$ ).

Table VIII. Stereochemistry and Its Temperature Dependence for the Reaction

$$\text{trans-Cr(en)}_2(\text{DMF})_2^{3+} \begin{cases} \xrightarrow{k_{63}} \text{cis-Cr(en)}_2(\text{DMF})_2^{3+} \\ \xrightarrow{k_{67}} \text{Cr(en)}(\text{DMF})_4^{3+} + \text{en} \end{cases}$$

$T, ^\circ\text{C}$	Isosbestic points $\lambda, \epsilon$ (nm, $M^{-1} \text{cm}^{-1}$ )		$R^f$	% <i>cis</i> -Cr(en) <sub>2</sub> (DMF) <sub>2</sub> <sup>3+</sup> in products <sup>g</sup>
	Obsd <sup>b</sup>	Calcd <sup>c</sup>		
66.6	554, 32.7	554, 32.7	4.25	81
40.1	424.5, 29.0	424.5, 29.2	6.7	87
	547, 38.4	547, 38.4		
25.0 <sup>d</sup>	422, 28.0	422, 28.4		100
	544, 40.0	543, 40.6		
	414, 26.6	414, 26.0 <sup>e</sup>		
	430, 31.0	430, 30.7 <sup>e</sup>		

<sup>a</sup> Two temperature extremes examined. <sup>b</sup> Another isosbestic point at  $\sim 335$  nm is not well defined. <sup>c</sup> Combined isosbestic point and spectral analysis data used to derive numbers in the fourth and fifth columns ( $\pm 2\%$ ). Average product ratio ( $R$ ) used to calculate isosbestic points. <sup>d</sup> Catalyzed path (see Discussion). Observed isosbestic points independent of temperature in this instance. <sup>e</sup> Note that these two isosbestic points merge as a higher proportion of Cr(en)(DMF)<sub>4</sub><sup>3+</sup> is found in the products. <sup>f</sup>  $R = k_{63}/k_{67}$ . <sup>g</sup>  $10^2 R/(1 + R)$ .

producible, the rate data and activation parameters (Table VII) are less precise than for some of the other reactions.

**Added Bromide Reactions.** Changes in absorption spectra are not explicable in terms of any of the known complexes reported for this system; this precluded the determination of rate and stereochemical data for reaction in the presence of N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>Br. However, up to  $1t_{1/2}$  the spectral changes were reproducible suggesting a well-defined reaction (and not solvent decomposition); this is probably ethylenediamine loss.

**III. *trans*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> → *cis*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> and Cr(en)(DMF)<sub>4</sub><sup>3+</sup> + en. Stereochemistry.** Despite the loss of ethylenediamine for this reaction even in the absence of bromide, this reaction is "clean" in that only two species *cis*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> and Cr(en)(DMF)<sub>4</sub><sup>3+</sup>(+en) are formed and in a strictly constant but kinetically controlled proportion over at least  $2t_{1/2}$  (Figures 5 and 6). This conclusion derives from complete spectral analysis for a three-component system and is confirmed by the isosbestic point data (Table VIII). As with the *trans*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup> reaction, catalysis was observed under some conditions. Interestingly, only the isomerization path was susceptible to this catalysis (Table VIII).

The *cis* to *trans* isomerization could not be precisely studied commencing with *cis*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> since the equilibrium strongly favors the *cis* isomer (90%). However, despite the small changes in spectra, it was clear that the initial reaction was simple isomerization. Ethylenediamine loss is not observed since the *cis* complex is thermodynamically stable with respect to the loss of amine.

**Kinetics.**  $k_0 (=k_{63} + k_{67})$  was calculated by methods similar to those described above for the *trans*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup> reaction. The individual  $k_{63}$  and  $k_{67}$  values were calculated as follows: (i) from  $k_0$  and the known product ratio ( $k_{63}/k_{67}$ )

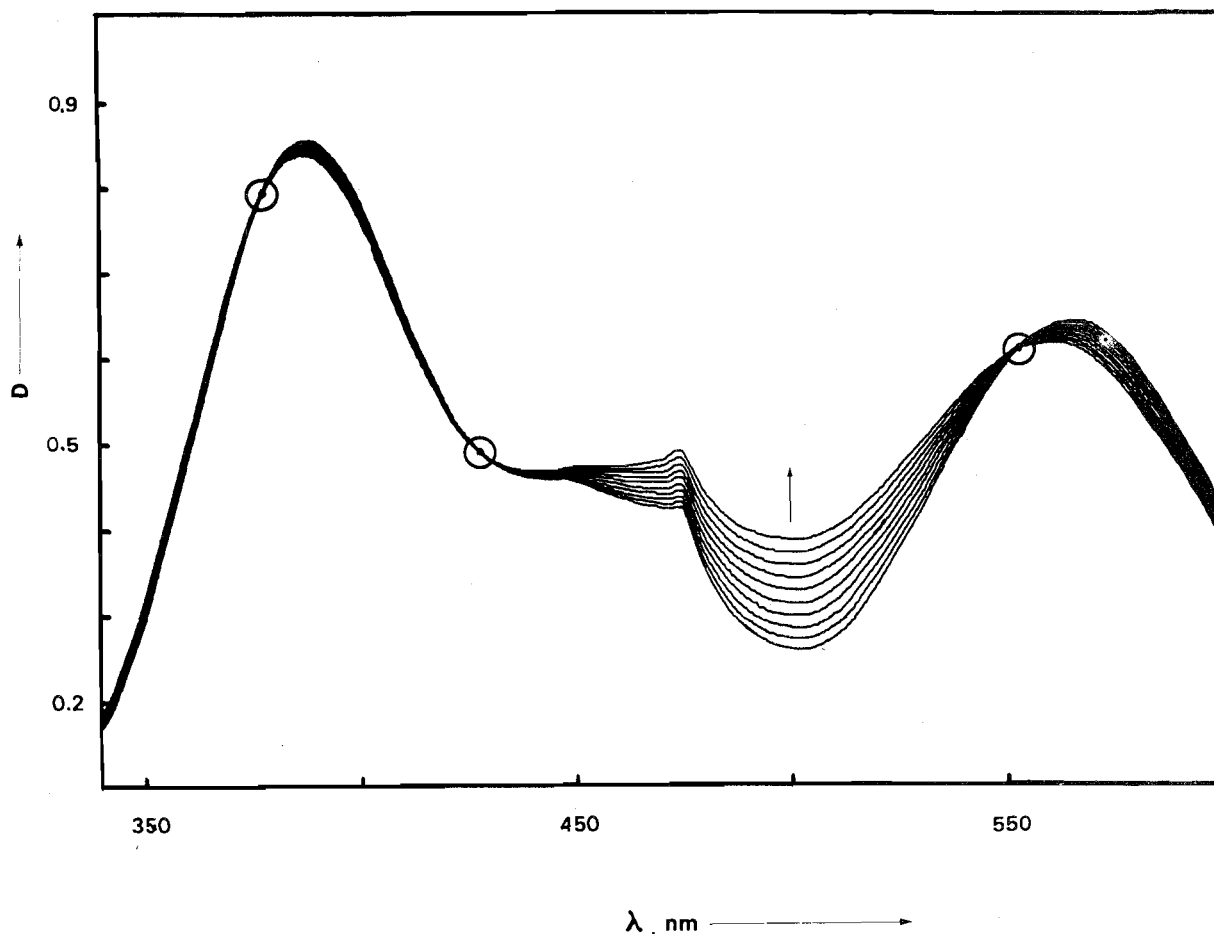


Figure 3. Absorbance changes for the reaction of *trans*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup> in DMF. [Complex]<sub>0</sub> = 1.50 × 10<sup>-2</sup> M, T = 55°, [N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>-Br]<sub>0</sub> = 0.

Table IX. First-Order Rate Constants for the Solvolysis and Isomerization Reactions

T, °C	<i>trans</i> -Cr(en) <sub>2</sub> (DMF) <sub>2</sub> <sup>3+</sup> $\xrightleftharpoons[k_{67}]{k_{63}}$ <i>cis</i> -Cr(en) <sub>2</sub> (DMF) <sub>2</sub> <sup>3+</sup> $\xrightarrow{k_{67}}$ Cr(en)(DMF) <sub>4</sub> <sup>3+</sup> + en			
	10 <sup>3</sup> [complex] <sub>0</sub> , <sup>a</sup> M	10 <sup>5</sup> k <sub>0</sub> , <sup>d</sup> sec <sup>-1</sup>	10 <sup>5</sup> k <sub>63</sub> , <sup>e</sup> sec <sup>-1</sup>	10 <sup>5</sup> k <sub>67</sub> , <sup>f</sup> sec <sup>-1</sup>
39.35	14.3	2.43 <sup>b</sup>	2.12 <sup>b</sup>	0.31 <sup>b</sup>
40.1	8.63	2.05	1.78	0.27
44.4	10.8	6.30 <sup>b</sup>	5.42 <sup>b</sup>	0.88 <sup>b</sup>
49.9	9.85	9.50	8.07	1.43
55.9	9.44	18.0	15.0	3.0
60.5	10.7	29.5 <sup>b</sup>	24.2 <sup>b</sup>	5.3 <sup>b</sup>
60.9	8.49	23.0	18.8	4.2
61.0	8.88	21.8	17.8	4.0
61.0	8.49	26.2 <sup>b</sup>	21.5 <sup>b</sup>	4.7 <sup>b</sup>
62.7	12.5	35.0	28.7	6.3
66.6	12.1	55.5	44.7	10.8
66.5	10.3		5.7 <sup>c</sup>	

<sup>a</sup> [Br<sup>-</sup>]<sub>0</sub> = 0. <sup>b</sup> Catalyzed. <sup>c</sup> Cis to trans rate (k<sub>36</sub>) estimated by initial rate method (±20%); *cis*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> starting complex. <sup>d</sup> k<sub>0</sub> = k<sub>63</sub> + k<sub>67</sub>; ±5%. <sup>e</sup> ±8%. <sup>f</sup> ±20%.

or (ii) directly from absorbance data collected at the *cis*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup>-*trans*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> (k<sub>67</sub>) and Cr(en)(DMF)<sub>4</sub><sup>3+</sup>-*trans*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> (k<sub>63</sub>) isosbestic points. In this second procedure two separate rate plots give k<sub>63</sub> and k<sub>67</sub> directly, but the results of this approach are less precise because the method<sup>16</sup> necessarily involves extrapolation of curved rate plots to t = 0, and the spectral changes at these wavelengths are not large. Rate constants calculated by the first method are given in Table IX and activation parameters in Table X.

**Added Bromide Reactions.** The addition of N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>Br

Table X. Activation Parameters for the Reactions

Rate constant <sup>a,b</sup>	<i>trans</i> -Cr(en) <sub>2</sub> (DMF) <sub>2</sub> <sup>3+</sup> $\xrightleftharpoons[k_{67}]{k_{63}}$ <i>cis</i> -Cr(en) <sub>2</sub> (DMF) <sub>2</sub> <sup>3+</sup> $\xrightarrow{k_{67}}$ Cr(en)(DMF) <sub>4</sub> <sup>3+</sup> + en				
	10 <sup>5</sup> k (50°), sec <sup>-1</sup>	ΔG <sup>‡</sup> (50°), kcal mol <sup>-1</sup>	E <sub>a</sub> , <sup>c</sup> kcal mol <sup>-1</sup>	ΔH <sup>‡</sup> , <sup>c</sup> kcal mol <sup>-1</sup>	ΔS <sup>‡</sup> , cal mol <sup>-1</sup> deg <sup>-1</sup>
k <sub>0</sub>	8.6	25.0	23.4	22.7	-7.0
k <sub>63</sub>	7.3	25.1	23.7	23.0	-6.5
k <sub>67</sub>	1.3	26.2	27.1	26.4	+1.0

<sup>a</sup> k<sub>0</sub> = k<sub>63</sub> + k<sub>67</sub>. <sup>b</sup> [Br<sup>-</sup>]<sub>0</sub> = 0. <sup>c</sup> ±1.0 kcal mol<sup>-1</sup> (k<sub>0</sub>); ±1.5 kcal mol<sup>-1</sup> (k<sub>63</sub>); ±2.0 kcal mol<sup>-1</sup> (k<sub>67</sub>).

to *trans*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> in DMF resulted in the crystallization of the very insoluble tribromide salt. However, studies on dilute (and supersaturated) solutions indicated quite clearly that ethylenediamine loss was still significant, and since we have not characterized bromomono(ethylenediamine)chromium(III) complexes, these reactions were not studied further beyond noting the reproducible spectral changes and the appearance of at least one new light-absorbing species.

**IV. Equilibria.** Results obtained under various conditions are given in Table XI. At zero bromide, some (10%) *trans*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> is present but only *cis*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> and *cis*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> (>98% of the total Cr) are found under all other conditions. Higher temperatures favor the *cis*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> complex. The equilibria are reproducible (±2%) commencing with any of the three *cis* complexes (1, 2, or 3) but not with any of the three *trans* isomers (4, 5, or 6), except under catalytic conditions; solvent decomposition becomes the dominant reaction at the later stages of the very slow *trans*-solvento complex reactions. The

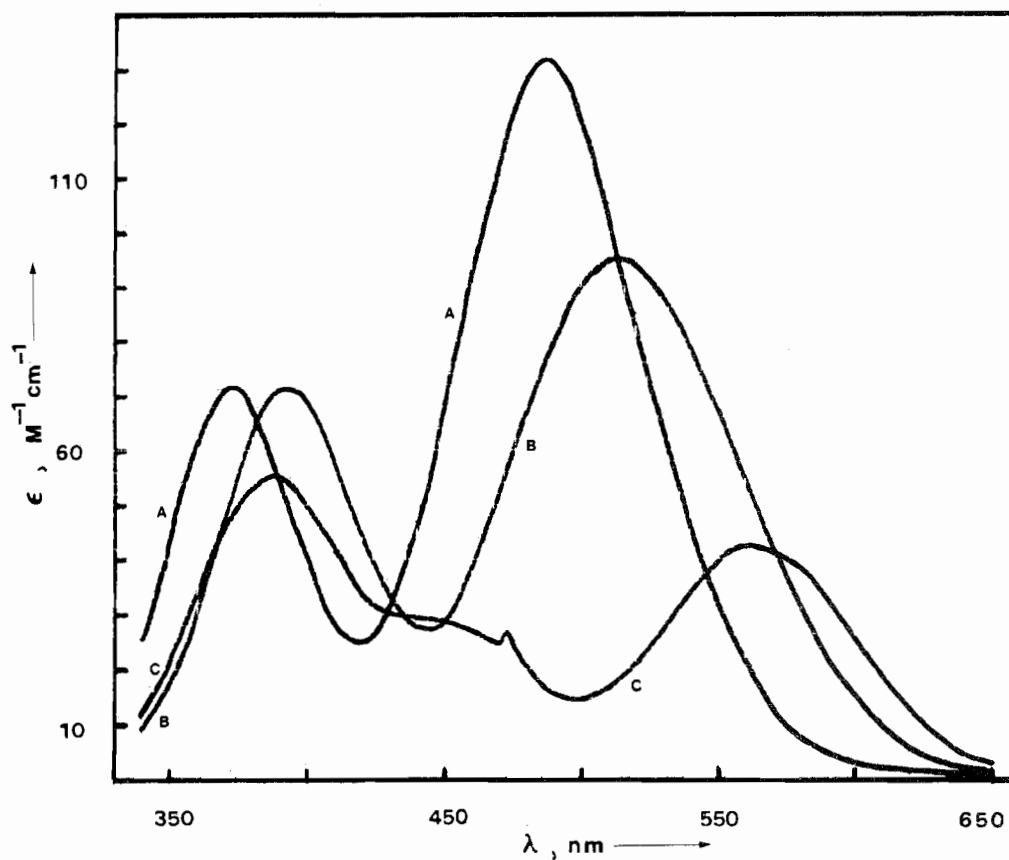


Figure 4. Pure absorption spectra in DMF at 25°: A, *cis*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup>; B, *cis*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup>; C, *trans*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup>.

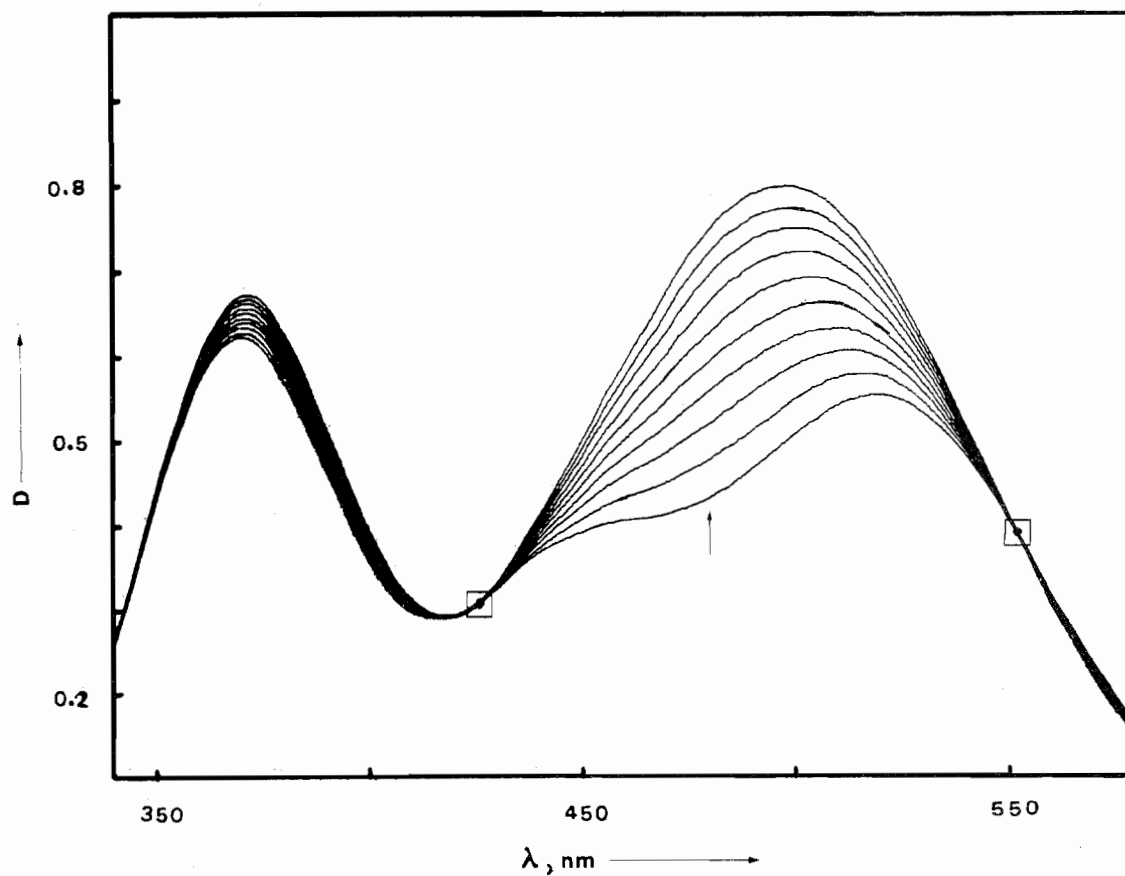


Figure 5. Absorption spectrum changes for the solvolysis and isomerization of *trans*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> in DMF. [Complex]<sub>0</sub> = 9.45 × 10<sup>-3</sup> M, T = 56°, [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>Br]<sub>0</sub> = 0.

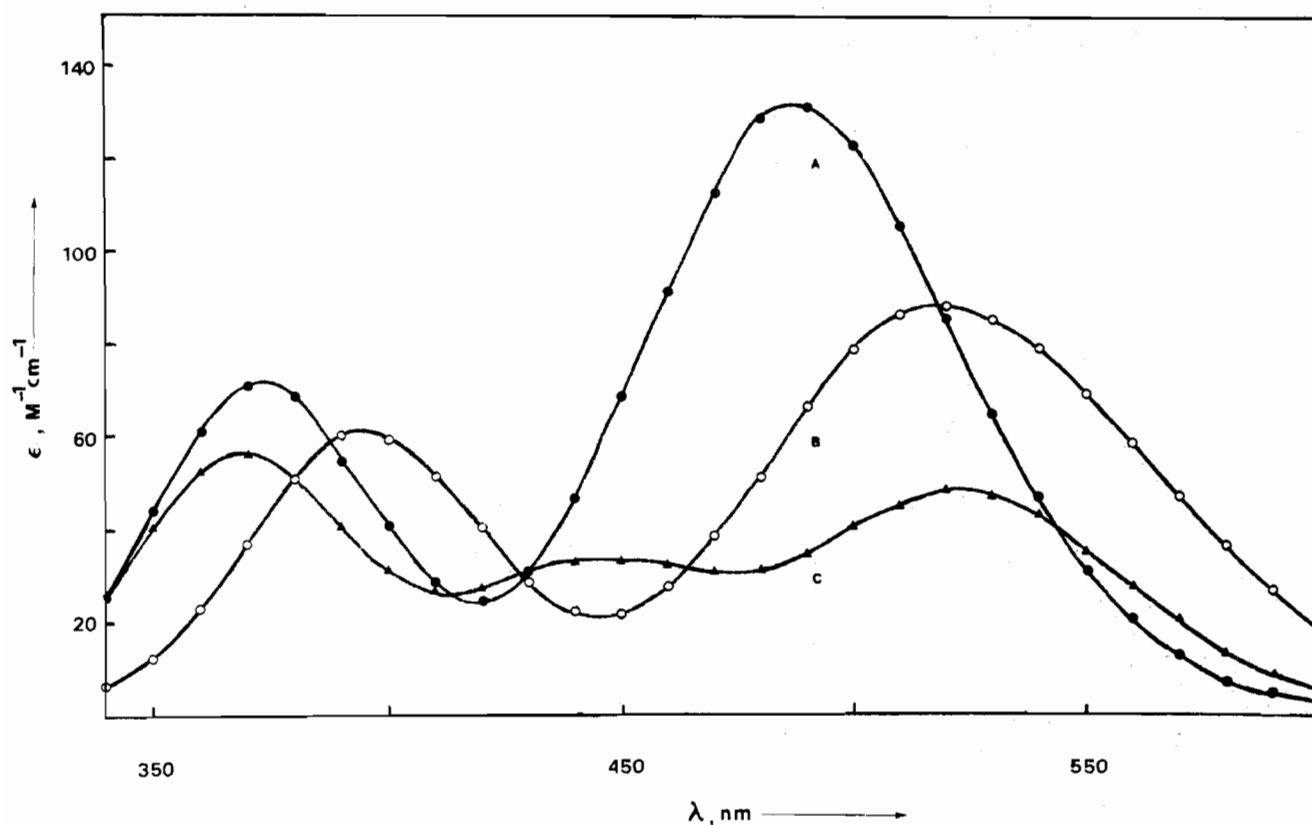


Figure 6. Pure absorption spectra in DMF at 25°: A (●), *cis*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup>; B (○), Cr(en)(DMF)<sub>4</sub><sup>3+</sup>; C (▲), *trans*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup>.

inability to reproduce the equilibria commencing with the *trans* isomers is not a direct consequence of the ethylenediamine loss found in these reactions since we know that the diamine is completely reassociated under equilibrium conditions. Thus Cr(en)(DMF)<sub>4</sub><sup>3+</sup> when equilibrated in DMF with 1 equiv of ethylenediamine at 60° yielded a 90:10 mixture of *cis*- and *trans*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup>, respectively, with little or no residual mono(ethylenediamine) complex. No disproportionation was observed. Significant solvent decomposition was not observed despite the long time period required for this equilibration; relatively rapid solvent decomposition is peculiar to reactions commencing with the *trans*-solvent complexes, suggesting that in some way they catalyze the breakdown of the solvent.

### Discussion

The kinetically significant reaction paths in the complete dibromo Cr(III)-DMF system are now established by this and previous work<sup>1</sup> (Figure 1). The analogous DMSO system is similar,<sup>3,4,7</sup> and we now turn to the discussion of the DMF results and to a comparison with the DMSO work.

**I. *cis*-Cr(en)<sub>2</sub>(DMF)Br<sub>2</sub><sup>2+</sup> ⇌ *cis*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> + Br<sup>-</sup> (*k*<sub>23</sub>, *k*<sub>32</sub>). Stereochemistry.** The forward and reverse reactions proceed with strict retention of configuration for both the free ion (*cis*-(DMF)Br<sub>2</sub><sup>2+</sup>) and the ion associated substrates (*cis*-(DMF)Br<sub>2</sub><sup>2+</sup> and *cis*-(DMF)<sub>2</sub><sup>3+</sup>). This stereochemical result is typical of Cr(III) substitution.<sup>22</sup> Identical behavior is found for the analogous DMSO reactions<sup>3</sup> except for the *cis*-Cr(en)<sub>2</sub>(DMSO)Br<sub>2</sub><sup>2+</sup> complex which at low [Br<sup>-</sup>]<sub>0</sub> is reported to give some 5% *trans*-Cr(en)<sub>2</sub>(DMSO)<sub>2</sub><sup>3+</sup> product.

**Kinetics.** The rate of *cis*-Cr(en)<sub>2</sub>(DMF)Br<sub>2</sub><sup>2+</sup> solvolysis (*k*<sub>23</sub>) is not detectably bromide dependent (Tables II and III) even at higher concentrations (6.5 × 10<sup>-2</sup> M) where complete ion pairing and significant ion triplet formation are expected for a doubly charged dipolar *cis* complex with bromide ion in DMF.<sup>18</sup> Compensatory effects of ground and transition state free energy modification through ion association have been seen previously.<sup>1,4</sup> For the solvolysis of *cis*-Cr(en)<sub>2</sub>-

Table XI. Equilibrium Data for the System

<i>cis</i> -Cr(en) <sub>2</sub> (DMF)Br <sub>2</sub> <sup>2+</sup> ⇌ <i>cis</i> -Cr(en) <sub>2</sub> (DMF) <sub>2</sub> <sup>3+</sup> + Br <sup>-</sup>					
Reac-	10 <sup>3</sup> [com-	10 <sup>3</sup> [N(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> Br] <sub>0</sub> , M	10 <sup>3</sup> [Br <sup>-</sup> ] <sub>0</sub> , M	T, °C	% <i>cis</i> -Cr(en) <sub>2</sub> (DMF) <sub>2</sub> <sup>3+</sup> at equilibrium <sup>c</sup>
2	8.37	0	8.37	40.2	60
2	8.66	8.59	17.25	40.2	64
1	8.67	8.67	26.0	40.0	71
2	8.62	18.9	27.5	40.2	69
1	9.35	14.6	33.1	40.0	71
2	8.29	27.6	35.9	40.25	70
1	8.86	26.4	44.1	40.0	70
1	8.69	43.2	61.1	40.0	70
1	8.88	89.5	107.4	40.0	74
1	8.94	189.4	207.3	40.0	69
3	6.47	3.46	3.46	40.0	27
3	6.49	6.49	6.49	40.0	37
3	6.49	12.98	12.98	40.0	71
3	6.49	16.3	16.3	40.05	73
3	6.49	22.8	22.8	40.0	69
3	6.49	64.9	64.9	40.05	73
3	12.45	8.51	8.51	60.95	46
2	7.57	0	7.57	61.0	60
2	8.53	0	8.53	60.95	64
3	8.51	8.51	8.51	60.95	62
2	7.57	15.4	22.9	61.0	80
3	7.57	23.5	23.5	61.0	80
3	7.83	24.4	24.4	20.0	64
2	7.80	16.0	23.8	20.0	62
3	6.49	13.0	13.0	22.0	56
1	8.78	0	17.6	22.0	65
6	8.78	0	0	63.0	90 <sup>b</sup>
3	8.78	0	0	63.0	90 <sup>b</sup>
3	8.78	0	0	40.0	90 <sup>b</sup>

<sup>a</sup> 1 = *cis*-Cr(en)<sub>2</sub>Br<sub>2</sub><sup>2+</sup>, [Br<sup>-</sup>]<sub>0</sub> = [N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>Br]<sub>0</sub> + 2[complex]<sub>0</sub>; 2 = *cis*-Cr(en)<sub>2</sub>(DMF)Br<sub>2</sub><sup>2+</sup>, [Br<sup>-</sup>]<sub>0</sub> = [N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>Br]<sub>0</sub> + [complex]<sub>0</sub>; 3 = *cis*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup>, [Br<sup>-</sup>]<sub>0</sub> = [N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>Br]<sub>0</sub>. <sup>b</sup> Equilibrium % *cis* for *cis*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup>; no added bromide ion. No *trans*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> found in the presence of bromide. <sup>c</sup> ±1%.



(DMSO)Br<sup>2+</sup> in DMSO,<sup>3</sup>  $k_{23}$  was observed to decrease on ion association with bromide and this was explained in terms of a competition between associated bromide ion and solvent for entry into the complex (so called mass law retardation). Without bromide exchange data it is difficult to separate such an effect from that attributable solely to ion association since the ion pair can be less reactive in solvolysis even when bromide does not compete successfully. Finally, we note that the free-ion DMSO complex is more reactive than its DMF analog (by a factor of  $\sim 3$  at 40°), a general result noted previously,<sup>1</sup> and that both the DMSO and DMF complexes solvolyze more slowly than the parent *cis*-Cr(en)<sub>2</sub>Br<sup>2+</sup> complex (by a factor of  $\sim 10$ ). This latter result is also found for stepwise aquation,<sup>19</sup> suggesting d activation<sup>26</sup> in both stepwise aquation and solvolysis. The perhaps naive argument<sup>21</sup> asserts that dissociative charge separation requires more energy for a 2+ than for a 1+ complex and that this energetic requirement contributes significantly to the activation energy.

The bromide anation rate ( $k_{32}$ ) of *cis*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> shows a typical dependence upon [Br<sup>-</sup>]<sub>0</sub>.  $k_{32}$  continues to increase well beyond the [Br<sup>-</sup>]<sub>0</sub> expected for complete ion pairing ( $\sim 6.5 \times 10^{-3}$  M). A limiting rate is reached at  $\sim 20 \times 10^{-3}$  M. Clearly multiple ion associated species are formed and it is to be expected that an ion triplet will anate more rapidly than an ion pair since there are more bromide ions in the outer sphere of the complex which can compete successfully with solvent for entry into the complex. The observation of a limiting rate at  $\sim 20 \times 10^{-3}$  M bromide implies either equivalent reactivity of the higher ion aggregates (e.g., the ion triplet and ion quadruplet) or, less likely, it implies that a maximum bromide ion activity has been reached where the cationic source of bromide (N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub><sup>+</sup>) has begun to ion pair competitively.

We should emphasize that the specific effects of ion association and, to a lesser extent, ionic strength can modify the shape of these rate profiles. Moreover, the observed rate can in principle still depend upon [anion]<sub>0</sub> beyond the region corresponding to saturation of the cationic reactant through ion association. Detailed quantitative analysis of the anation of multiply charged complexes is complicated by overlapping ion association equilibria of the various ion aggregates each of which has a characteristic and generally different anation rate.

The DMF anation reaction shows a strong similarity to its DMSO counterpart. Indeed, the limiting bromide anation rate in DMF ( $\sim 12.5 \times 10^{-5}$  sec<sup>-1</sup>, 40°) is very nearly the same as that in DMSO ( $\sim 11.7 \times 10^{-5}$ , sec<sup>-1</sup>, 40°)<sup>3</sup> although both the substrates and solvents are different. However, the two limiting rates may refer to different ion multiplets; ion association in DMF is significantly greater than in DMSO.<sup>18</sup>

Finally we note that if the *cis*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup>–*cis*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> interconversion occurs in a single step (I process<sup>20</sup>), then we can assign an Ia mechanism for anation since by the principle of microscopic reversibility the solvolysis of the *cis*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup> complex (assigned as dissociative) must proceed through the same transition state. The same argument applies to the DMSO reactions<sup>3</sup> previously concluded to be dissociative.

**II. *trans*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup> → *cis*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup> ( $k_{52}$ ) and *cis*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> + Br<sup>-</sup> ( $k_{53}$ ). Kinetics and Stereochemistry.** Complexes **2** (35%) and **3** (65%) are the only observable products of this reaction in the absence of added bromide ion (see Figure 1). The proportion of **2** (*cis*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup>) is somewhat greater at higher temperatures. The equilibrium ratio of products is similar and seems to show a similar temperature dependence. However, it is apparent that each of the two products is *directly* formed since, particularly at an early stage of reaction (less than 1 $t_{1/2}$ ), product

interconversion is too slow to account for the constant product ratio on the basis of exclusive *cis*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup> or *cis*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> formation followed by "instantaneous" equilibration. Product interconversion might have been expected to be evident as a shift in isobestic points after about 1 $t_{1/2}$  of *trans*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup> reaction since this is 3–5 times as fast as the initial reaction. However, the isobestic points remain sharp since the equilibrium distribution percentage closely corresponds to the kinetic proportions at all temperatures investigated.

*trans*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> was not observed at any stage of the *trans*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup> reaction. This species can be excluded as both a solvolysis and isomerization reaction intermediate (<5%) since the rate of *trans*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> consumption in DMF is only 3 times as fast as the *trans*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup> rate; therefore *trans*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup>, if formed, would accumulate in sufficient quantity to be detected. Note also that *trans*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> releases ethylenediamine; no diamine loss was observed ([Br<sup>-</sup>]<sub>0</sub> = 0) in the *trans*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup> reaction. We therefore conclude that the solvolysis of *trans*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup> in DMF is significantly nonretentive (i.e.,  $k_{53} \gg k_{56}$ ); this is extremely unusual for Cr(III) substitution.<sup>22</sup> Note that this reaction must proceed *via* a different path to the Hg<sup>2+</sup>-, Tl<sup>3+</sup>-, and Ag<sup>+</sup>-promoted solvolyses which are strictly retentive.<sup>2,7</sup> In contrast to the DMF system, *trans*-Cr(en)<sub>2</sub>(DMSO)Br<sup>2+</sup> isomerization is the exclusive initial reaction ( $k_{52} \gg k_{53}$ ) in DMSO and so the direct solvolysis path is not observable.<sup>3</sup> The metal ion induced solvolyses are however observable and proceed with retention.<sup>7</sup>

It is striking that the rates of isomerization ( $k_{52}$ ) of the *trans*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup> and *trans*-Cr(en)<sub>2</sub>(DMF)Cl<sup>2+</sup> <sup>7</sup> complexes in DMF are very nearly identical. This suggests a common isomerization mechanism.

Rate-determining halide solvolysis would seem to be excluded since the bromo complex would be expected to be considerably more reactive (by a factor of  $\sim 30^1$ ) unless the stereochemistry of reentry of dissociated chloride and bromide were vastly different. A similar situation pertains in the DMSO system.<sup>3,4,7</sup> The results strongly suggest that isomerization proceeds *via* dissociation of a neutral leaving group. Watts has reached a similar conclusion based on other evidence and has suggested that isomerization occurs *via* solvent exchange.

It is possible, if not probable, that the rate of Cr–N bond cleavage is comparable to the very slow rate of *trans*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup> reaction. Therefore isomerization may well proceed *via* dissociation and rechelation of the ethylenediamine chelate although no net loss of amine is observed. The observation that the addition of bromide ion promotes en release therefore assumes especial significance. There is no *a priori* reason that the Cr–N bond should suddenly become "activated" in the presence of added bromide ion. It is well known that halide ion interacts with amino protons<sup>18</sup> and thus ion-associated bromide can effect the rechelation process such that the participation of the chelate in reaction is then evident as a loss of en. In contrast to our results, neither bromide nor chloride promotes en loss from *trans*-Cr(en)<sub>2</sub>(DMSO)Br<sup>2+</sup> in DMSO,<sup>4</sup> although other similar systems show this curious phenomenon.<sup>4,7</sup>

We should point out that if en is dissociating from the *trans*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup> complex, ring closure can accomplish both isomerization ( $k_{52}$ ) and nonretentive bromide solvolysis ( $k_{53}$ ), as is observed; there would be no need to postulate the formation of an intermediate which involves a significant rearrangement of molecular framework, a decidedly unfavorable energetic requirement in Cr(III) substitution.<sup>22</sup>

**III. *trans*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> → *cis*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> ( $k_{63}$ )**



and Cr(en)(DMF)<sub>4</sub><sup>3+</sup> + en (*k*<sub>67</sub>). **Stereochemistry and Kinetics.** This reaction gives the two complexes shown in a constant proportion. en loss is more important at higher temperatures. Unlike the *trans*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup> reactions we have been able to deal quantitatively with the problem of en release since pure [Cr(en)(DMF)<sub>4</sub>](ClO<sub>4</sub>)<sub>3</sub> has been isolated and the system comprises no more than three complexes at any time.

It is especially interesting to note that the Cr(en)(eN)-(DMF)<sub>3</sub><sup>3+</sup> complex<sup>23</sup> does not accumulate; this contrasts with analogous aqueous systems where such "one-ended" chelate (eN) complexes usually appear in Cr-N bond cleavage reactions, presumably because of protonation of the Cr-eN moiety.<sup>24</sup> This important result implies that either cleavage of the second Cr-N bond or rechelation is faster than the initial ring opening. Results in aqueous systems<sup>22a,24</sup> and other work<sup>7</sup> suggest that fast rechelation is the effective process. Since in rechelation there is no obvious stereochemical preference for *cis*- or *trans*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> (though see ref 24b), we suggest that isomerization occurs in this way, although we cannot exclude a simple solvent-exchange mechanism of isomerization.

We<sup>7</sup> and others<sup>4</sup> have examined the analogous reactions of the *trans*-Cr(en)<sub>2</sub>(DMSO)<sub>2</sub><sup>3+</sup> complex in DMSO; the results are quite similar to those for DMF.<sup>7</sup> We have not been able to follow the *trans*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> reaction much beyond 2*t*<sub>1/2</sub> due to catalysis and solvent decomposition problems<sup>25</sup> mentioned earlier, but we may comment on results obtained for subsequent reaction in the DMSO system.<sup>7</sup> There rechelation of the initially released en (~15%) is found to occur only after about (4-5)*t*<sub>1/2</sub> of reaction; therefore en entry into Cr(en)(DMSO)<sub>4</sub><sup>3+</sup> must be at least 5 times slower than the initial *trans*-Cr(en)<sub>2</sub>(DMSO)<sub>2</sub><sup>3+</sup> reaction. Almost complete rechelation (95%, 60°) as the *cis*-Cr(en)<sub>2</sub>(DMSO)<sub>2</sub><sup>3+</sup> complex ultimately occurs. A similar situation must exist for the DMF system since we know en is completely chelated under equilibrium conditions yet the Cr(en)(DMF)<sub>4</sub><sup>3+</sup> complex shows no evidence of reaction with conformed en at least up to 2*t*<sub>1/2</sub> of *trans*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> reaction.

Finally we note that the very slow isomerization of the *cis*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> complex to the *trans* isomer (only ~10% reaction) must occur *via* the same path as the reverse reaction. No en loss was observed since *cis*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> is stable with respect to Cr(en)(DMF)<sub>4</sub><sup>3+</sup> + en under the conditions.

**IV. Equilibria.** There are four essential features of the equilibrium results. First, the system is dominated by the mono- and bis(solvento) complexes. Even at high [Br<sup>-</sup>]<sub>0</sub>, there is no detectable dibromo complex. The DMSO system is identical except that there is a higher proportion of bis(solvento) complex. More extensive solvolysis in DMSO (over DMF) is observed in Co(III) and other Cr(III) systems and it is also generally found that the Cr(III) systems show greater proportions of solvento complexes in both DMF and DMSO. This is especially true of the dibromo system reported here (DMF) and for DMSO.<sup>3</sup> These results may be attributed to the greater stability of Cr(III) complexes with oxygen donor solvents<sup>1-3,5,6</sup> and to an inherently weak Cr-Br bond.<sup>1,22a</sup>

Second, the equilibria are dominated by *cis*-solvento complexes. At [Br<sup>-</sup>]<sub>0</sub> = 0, we find 90% *cis*- and 10% *trans*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> (60°); at higher [Br<sup>-</sup>]<sub>0</sub>, the bromo and bis(solvento) isomers are exclusively *cis*. No *trans*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup> was observed under any conditions. In the analogous DMSO system<sup>3</sup> we find<sup>7</sup> exclusively *cis* isomers throughout the complete bromide range. Watts has established previously that this aspect of the equilibria is not metal dependent; *cis* geometry is stabilized through preferential dipolar solvation and its greater ion association in these strongly dipolar solvents.<sup>18</sup> The literature is too extensive to cite here, but we

have observed almost invariably that increasing the formal charge on the complex also leads to *cis* stabilization; this is true even in less polar solvent systems such as water and methanol—hence the predominance of 2+ halo(aquo) and 3+ diaquo *cis* isomers found in equilibrated aqueous systems.

Third, the DMF equilibria show their significant bromide dependence at somewhat lower concentrations than in the corresponding DMSO system. This follows from the established<sup>18</sup> greater ion association in DMF. The equilibrium *cis*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup> proportion reaches a limit at [Br<sup>-</sup>]<sub>0</sub> = 30 × 10<sup>-3</sup> M whereas this limit occurs at [Br<sup>-</sup>]<sub>0</sub> = 45 × 10<sup>-3</sup> M in the DMSO system at the same temperature (40°) and at a similar [complex]<sub>0</sub>. Moreover, the observation of a limiting equilibrium distribution in both systems indicates that ion-associated bromide is as stable as coordinated bromide under these conditions; the proportion of bromo(solvento) complex would otherwise increase hyperbolically as the [Br<sup>-</sup>]<sub>0</sub> was increased.

Finally, we should comment on the apparent stability of the Cr(en)<sub>2</sub> moiety with respect to en solvolysis in DMF; Cr(en)(DMF)<sub>4</sub><sup>3+</sup>(+en) is not detectable at equilibrium (*i.e.*, <2%) whereas in DMSO, which seems to be a better ligand,<sup>1</sup> some Cr(en)(DMSO)<sub>4</sub><sup>3+</sup>(+en) is found (5%).<sup>7</sup> The latter result is important because it suggests that the bis(ethylenediamine) complex in DMF, as in DMSO, is only *just* stable to loss of en. These observations are consistent with a relatively weak Cr-N bond<sup>22a</sup> which undoubtedly is connected with the often noted amine-cleavage reactions in aqueous<sup>22a</sup> as well as nonaqueous media (this work and ref 7).

There is evidence to suggest that amine cleavage reactions should be more important in very slow reactions,<sup>7</sup> such as those of the *trans*-solvento complexes described in this work. Thus, since we have shown that en complexes have measurable stability in the thermodynamic sense in DMF and DMSO, reactions such as halide solvolysis or isomerization, possibly dominated by chelate participation, may well appear "normal" in the sense that net loss of amine is not observed. We are directing future experiments to clarify the role of the chelate in Cr(III) substitution.

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**Registry No.** *cis*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup>, 46935-03-9; *cis*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup>, 46361-63-1; *cis*-Cr(en)<sub>2</sub>Br<sup>2+</sup>, 20631-53-2; *trans*-Cr(en)<sub>2</sub>(DMF)Br<sup>2+</sup>, 46361-62-0; *trans*-Cr(en)<sub>2</sub>(DMF)<sub>2</sub><sup>3+</sup>, 29845-00-9; Cr(en)(DMF)<sub>4</sub><sup>3+</sup>, 53586-56-4; [Cr(en)(DMSO)<sub>4</sub>](ClO<sub>4</sub>)<sub>3</sub>, 53586-58-6.

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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*- $\text{Cr}(\text{en})_2(\text{DMF})\text{Cl}^{2+}$  isomerizes completely to the *cis* isomer in dimethylformamide (DMF);  $k_{\text{tc}} = 2.2 \times 10^{-5} \text{ sec}^{-1}$  ( $50^\circ$ ),  $\Delta H^\ddagger = 24.4 \text{ kcal mol}^{-1}$ , and  $\Delta S^\ddagger = -4.5 \text{ cal mol}^{-1} \text{ deg}^{-1}$ . Similarly, *trans*- $\text{Cr}(\text{en})_2(\text{DMSO})\text{Cl}^{2+}$  isomerizes to its *cis* form in dimethyl sulfoxide (DMSO);  $k_{\text{tc}} = 3.7 \times 10^{-5} \text{ sec}^{-1}$  ( $50^\circ$ ),  $\Delta H^\ddagger = 22.3 \text{ kcal mol}^{-1}$ , and  $\Delta S^\ddagger = -10.0 \text{ cal mol}^{-1} \text{ deg}^{-1}$ . In the absence of added chloride ion and at lower temperatures ( $<60^\circ$ ), 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*- $\text{Cr}(\text{en})_2(\text{DMSO})_2^{3+}$  is found while there is no detectable chloride loss from the *cis*- $\text{Cr}(\text{en})_2(\text{DMF})\text{Cl}^{2+}$  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*- $\text{Cr}(\text{en})_2\text{Cl}^{2+}$  in DMF and DMSO.

### Introduction

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

### Experimental Section

**Complexes.** *cis*- and *trans*- $[\text{Cr}(\text{en})_2(\text{DMF})\text{Cl}](\text{ClO}_4)_2$ , *trans*- $[\text{Cr}(\text{en})_2(\text{DMSO})\text{Cl}](\text{ClO}_4)_2$ , *cis*- $[\text{Cr}(\text{en})_2(\text{DMSO})\text{Cl}](\text{NO}_3)\text{ClO}_4$ , *cis*- $[\text{Cr}(\text{en})_2(\text{DMF})_2](\text{ClO}_4)_3$  (and *cis*- $[\text{Cr}(\text{en})_2(\text{DMF})_2]\text{NO}_3(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ ), and *cis*- $[\text{Cr}(\text{en})_2(\text{DMSO})_2](\text{ClO}_4)_3$  were from batches used in concurrent work; complete characterization is given elsewhere.<sup>2</sup> All complexes used were freshly prepared.<sup>5</sup>

**Solvents, Other Materials, and Kinetic Technique.** Full details have been described.<sup>2,9</sup> All reactions were followed spectrophotometrically on an automatic recording Hitachi EPS-3T instrument by the continuous-scan technique. First-order rate constants were calculated

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

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

<sup>a</sup>  $\lambda$ , nm;  $\epsilon$ ,  $M^{-1} \text{ cm}^{-1}$ . <sup>b</sup> Also an ill-defined isosbestic point in the range 350–360 nm. <sup>c</sup>  $T = 64^\circ$ ; temperature dependent. <sup>d</sup> Close to an "isosbestic line," 430–445 nm. <sup>e</sup>  $T = 40^\circ$ ; temperature dependent.

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.<sup>2a</sup>

### Results

**Isomerization of *trans*- $\text{Cr}(\text{en})_2(\text{DMSO})\text{Cl}^{2+}$  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)  $\text{Cl}^-$  loss from the *cis* product occurs after several  $t_{1/2}$ 's and does not interfere. We note that, at the highest temperature studied ( $68^\circ$ ), 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,<sup>2b</sup> 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 ( $\pm 2\%$ ) for  $k_{\text{tc}}$  was obtained for calculations made at