and r indicate the relative conformation of the two rings of the pair, m if the two rings are both δ or both λ and r if one is δ while the other is λ.

(27) The geometry of the five-membered rings used for this computation was obtained following the algorithm presented earlier[16] and using the bond length and angle data of the E1 and G1 rings of the observed H_3Cu^{II}DTPA complex. Since the bond lengths and angles of a five-membered chelate ring can vary considerably, the numbers given should be used with caution. They are meant to give gross, qualitative tendencies rather than exact, quantitative measures.

(28) With small metal ions, the axial G rings can be quite flat. In this case, the distinction between the ar and am types disappears, the interplanar angle will be intermediate between those for the ar and am types, and the preferred configuration will be cis.

(29) D. A. Buckingham, I. E. Maxwell, A. M. Sargeson, and M. R. Snow, *J. Amer. Chem. Soc.*, **92**, 3617 (1970).

(30) The comparison to the Cu^{II}–EDTA structure is complicated by the fact that the E and G rings in this structure span axial ligands, *i.e.*, the terminal ligands of this ring pair form long bonds to the copper ion under the possible influence of the Jahn–Teller effect.[24] In contrast, the E1 and G1 rings of the present DTPA structure lie on the equatorial plane and their ligand atoms form normal bonds to the copper ion. We compare the ring angle sums of the E1 and G1 rings of the DTPA structure to those of the E and G rings of the EDTA structure, but the bond lengths Cu–O_1, Cu–N_1, and Cu–N_2 of the DTPA structure are compared to the equatorial bonds of the R rings of the EDTA structure.

(31) N. V. Novozhilova, T. N. Polynova, M. N. Porai-Koshits, and L. I. Martynenko, *Zh. Strukt. Khim.*, **8**, 553 (1967).

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Kinetics and Stereochemistry of Solvolysis of *cis*- and *trans*-Dibromo- and Bromochlorobis(ethylenediamine)chromium(III) Complexes in Dipolar Aprotic Solvents

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The primary solvolysis of bromide ion from each of the *cis*- and *trans*-dibromobis(ethylenediamine)chromium(III) cations occurs completely and with steric retention in dimethylformamide. Both cis and trans isomers of the product bromo(dimethylformamide) complex have been isolated. The rates and equilibria have been studied and were found not to be significantly dependent upon the concentration of added bromide ion, despite considerable ion pairing of the ground-state reactants (established independently). Activation parameters have been measured. For the bromochloro isomers in dimethylformamide and dimethyl sulfoxide, solvolysis of bromide is much faster than that of chloride and is measurably reversible. The reactions in both solvents are quite analogous to those of the dibromo complexes, but they yield exclusively the isomeric chloro(solvento) complexes as products in these cases. Again, both the cis and trans isomers of the product complexes $Cr(en)_2(DMF)Cl^{2+}$ and $Cr(en)_2(DMSO)Cl^{2+}$ have been isolated. For these and related reactions, cis:trans and bromide:chloride rate ratios and the qualitative effect of solvent transfer on these are shown to be consistent with a common dissociative mechanism.

Introduction

The present work was initiated as part of a more general program concerned with chromium(III) substitution reactions in relation to their well-studied cobalt(III) analogs. This and subsequent publications will describe the kinetics and stereochemistry of bis(ethylenediamine)- and tetraamminechromium(III) complexes in dipolar aprotic media. Watts, *et al.*, have recently reported on the reactions of the dichlorobis(ethylenediamine)chromium(III) complexes in dimethylformamide (DMF)[1] and dimethyl sulfoxide (DMSO)[2,3] and the analogous dibromo cations in DMSO.[4] Moreover, an independent study of the important ion-pairing process for a wider range of such chromium(III) complexes in dipolar aprotic media has been reported.[5] In this paper we consider the primary solvolysis reactions of the *cis*- and *trans*-$Cr(en)_2Br_2^+$ ions in DMF and *cis*- and *trans*-$Cr(en)_2ClBr^+$ ions in both DMF and DMSO. Thus this work now completes the dichloro, dibromo, and bromochloro complex systems in these two solvents. The directly analogous cobalt(III) reactions have been studied.[8-12]

The reactions reported here for the solvolyses of the relatively labile bromide leaving group were expected to be uncomplicated by chromium–nitrogen cleavage side reactions which are often prevalent in aqueous and other nonaqueous Cr(III) systems.[6] The studies of the reactions of the *cis*- and *trans*-halo(solvento) and bis(solvento) complexes which complete this research are appropriately treated elsewhere[7] because parallel amine dissociation reactions are important there.

Experimental Section

Preparation of Complexes. *cis*- and *trans*-$[Cr(en)_2ClBr]Br\cdot H_2O$ and *cis*- and *trans*-$[Cr(en)_2ClBr]ClO_4$ were synthesized as described previously.[13]

A new, easier, and more convenient synthesis of *trans*-$Cr(en)_2ClBr^+$ is as follows. A hot, saturated solution (pink-red) of *trans*-$[Cr(en)_2(OH_2)Cl]Br_2$[13] in tetramethylene sulfone readily turns green at steam bath temperatures and then deposits fine green crystals of *trans*-$[Cr(en)_2ClBr]Br$. After complete reaction (approximately 10 min) acetone was added to complete crystallization. The product was collected and washed with acetone–water (1:1) and finally with ether. The yield is essentially quantitative. Deep green-blue needles of the monohydrate were obtained by recrystallization.[13] The perchlorate by metathesis in water (sodium perchlorate) was recrystallized from cold DMF by the slow addition of aqueous sodium perchlorate. *Anal.* Calcd for $[Cr(en)_2ClBr]Br\cdot H_2O$: C, 12.4; H, 4.7; N, 14.5; Br, 41.5; Cl, 9.2. Found (cis): C, 12.3; H, 4.8; N, 14.5; Br, 41.7; Cl, 8.6. Found (trans): C, 12.1; H, 4.7; N, 14.2; Br, 42.2; Cl, 9.0. Calcd for $[Cr(en)_2ClBr]ClO_4$: Cr, 13.4; C, 12.4; H, 4.1; N, 14.5; Br, 20.6; Cl, 18.3. Found (cis): Cr, 13.4; Br, 20.7; Cl, 18.1. Found (trans): Cr, 13.3; C, 12.3; H, 3.9; N, 14.0; Br, 20.8; Cl, 18.3.

Caution! Perchlorates are potentially explosive. For example, in our hands *cis*-$[Cr(en)_2Br_2]ClO_4$ has exploded violently on heating rapidly to 130°. Room-temperature drying is recommended.

cis-$[Cr(en)_2Cl_2]Cl\cdot H_2O$,[14,15] recrystallized from water–hydrochloric acid (10 *M*)–ethanol (1:1:1), was converted to the bromide ($\cdot H_2O$) and then to *cis*-$[Cr(en)_2Br_2]Br\cdot H_2O$ by a known method[16] modified as described now. An aquated *cis*-$Cr(en)_2Cl_2^+$ solution[16] ($Cr(en)_2(OH)_2{}_2^{3+}$) was taken to dryness three times with hydrobromic acid (48%) to yield completely chloride free $[Cr(en)_2Br_2]Br$. Very rapid evaporation is essential (<50°; rotary evaporation). Prepared in this way, traces of trans isomer are produced which are readily removed by recrystallization as the bromide salt from ice-cold DMF solution by the addition of cold aqueous sodium bromide. Fine shiny

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violet plates of the less soluble and pure *cis*-[Cr(en)$_2$Br$_2$]Br·H$_2$O were obtained in 75% yield. The perchlorate salt was obtained by a second crystallization from DMF using aqueous sodium perchlorate in place of bromide. Simple aqueous recrystallization is not recommended; the recovery is low (~10%) and *cis*-[Cr(en)$_2$(OH$_2$)Br]Br$_2$·H$_2$O[4,13] tends to crystallize unless the solution is seeded. Note that thermal deaquation[13] of the latter complex can give [Cr(en)$_2$Br$_2$]Br which is mainly but not exclusively cis. *trans*-[Cr(en)$_2$Br$_2$]Br·H$_2$O and *trans*-[Cr(en)$_2$Br$_2$]ClO$_4$ were prepared as described previously.[13] *Anal.* Calcd for [Cr(en)$_2$Br$_2$]Br·H$_2$O: Cr, 12.1; C, 11.2; H, 4.2; N, 13.0; Br, 55.8. Found (cis): Cr, 12.1; C, 11.4; H, 4.4; N, 13.2; Br, 55.8. Found (trans): Cr, 12.1; C, 11.2; H, 4.2; N, 13.2; Br, 55.3. Calcd for [Cr(en)$_2$Br$_2$]ClO$_4$: C, 11.1; H, 3.7; N, 13.0; Br, 37.0; Cl, 8.2. Found (cis): C, 11.6; H, 3.8; N, 13.0; Br, 37.1; Cl, 8.2. Found (trans): C, 11.4; H, 3.7; N, 12.7; Br, 37.0; Cl, 8.3.

cis- and *trans*-[Cr(en)$_2$(DMF)Br](ClO$_4$)$_2$, *trans*-[Cr(en)$_2$(DMF)Cl](ClO$_4$)$_2$, and *trans*-[Cr(en)$_2$(DMSO)Cl](ClO$_4$)$_2$ were freshly prepared by reported procedures.[13] *Anal.* Calcd for [Cr(en)$_2$(DMF)Br](ClO$_4$)$_2$: C, 16.1; H, 4.4; N, 13.4; Br, 15.3; Cl, 13.4. Found (cis): C, 16.1; H, 4.6; N, 13.3; Br, 15.2; Cl, 13.5. Found (trans): C, 16.0; H, 4.4; N, 13.2; Br, 15.4; Cl, 13.5. Calcd for [Cr(en)$_2$(DMF)Cl](ClO$_4$)$_2$: C, 17.5; H, 4.8; N, 14.6; Cl, 22.2. Found: C, 17.4; H, 4.9; N, 14.4; Cl, 22.2. Calcd for [Cr(en)$_2$(DMSO)Cl](ClO$_4$)$_2$: Cr, 10.7; C, 14.9; H, 4.5; N, 11.5; Cl, 22.0. Found: Cr, 10.7; C, 14.9; H, 4.5; N, 11.0; Cl, 22.1.

cis- and *trans*-[Cr(en)$_2$(DMSO)Br](ClO$_4$)$_2$, *cis*-[Cr(en)$_2$(DMSO)Cl]NO$_3$·ClO$_4$, and *cis*-[Cr(en)$_2$(DMF)Cl](ClO$_4$)$_2$ were prepared according to Palmer and Watts.[1,2,4] *Anal.* Calcd for [Cr(en)$_2$(DMSO)Br](ClO$_4$)$_2$: C, 13.6; H, 4.2; N, 10.6; Br, 15.1; Cl, 13.2; S, 6.0. Found (cis): C, 13.9; H, 4.2; N, 10.6; Br, 15.2; Cl, 13.2; S, 6.1. Found (trans): C, 13.8; H, 3.9; N, 10.7; Br, 15.1; Cl, 13.2; S, 6.1. Calcd for [Cr(en)$_2$(DMSO)Cl]NO$_3$·ClO$_4$: C, 16.1; H, 5.0; N, 15.7; Cl, 15.9; S, 7.2. Found: C, 16.0; H, 5.1; N, 16.0; Cl, 16.0; S, 7.2. Calcd for [Cr(en)$_2$(DMF)Cl](ClO$_4$)$_2$: C, 17.5; H, 4.8; N, 14.6; Cl, 22.2. Found: C, 17.6; H, 4.7; N, 14.9; Cl, 22.2.

Characterization. Isomeric purity was checked as described previously.[13,17,18] Freshly prepared salts (perchlorates) were generally used; this was found particularly important for the solvento complexes where deterioration after storage for a few weeks was often evident. Light was excluded as a routine precaution. Elemental analyses (C, H, N, S, Br, Cl) were performed by the Australian Microanalytical Service, CSIRO, Melbourne. Chromium was determined[13] by oxidation of the chromium(III) complex in hot alkaline hydrogen peroxide solution and measurement of the resultant chromate absorbance ($\epsilon_{372.5}$ 4815).

Solvents and Other Materials. DMSO and DMF were purified and dried according to Millen and Watts[19] (DMSO, d^{25} 1.0954, n^{25}D 1.4768; DMF, d^{25} 0.9441, n^{25}D 1.4301). Freshly distilled solvent was always used.[5] Tetraethylammonium bromide (BDH) was recrystallized twice from hot dimethylacetamide and stored *in vacuo* over anhydrous magnesium perchlorate. *Anal.* Calcd for [N(C$_2$H$_5$)$_4$]Br: C, 45.7; H, 9.6; N, 6.7; Br, 38.0. Found: C, 45.8; H, 9.5; N, 6.7; Br, 38.3. All other materials were reagent grade.

Kinetic Techniques. All rates were determined spectrophotometrically; the essential methods and instrumentation used have been previously described.[17,18] Routinely, DMF and DMSO solutions were kept under dry nitrogen. However, small amounts of water (~1% w/w) were shown to have no measurable effect on any of the reactions. Corrections for solvent expansion were made where necessary ($\gamma_{DMF} = 94.4$, $\gamma_{DMSO} = 88.4$ deg^{-1}). Free bromide and chloride were determined by standard potentiometric titration; solutions were freed of complex by passage through Dowex AG50W-X8 (100–200 mesh, H$^+$ form) cation-exchange resin at 0°. Blank experiments showed that the complex was quantitatively retained on the resin (DMSO, DMF, or semiaqueous solution may be used).

Table I. Isosbestic Point Data for the Solvolyses[a] Cr(en)$_2$Br$_2$$^+$-DMF → Cr(en)$_2$(DMF)Br^{2+} + Br$^-$

Reactant isomer	Isosbestic points λ (ε)[b] Obsd	Calcd for 100% steric retention
Cis	529 (89.5)	529 (89.0)
	458 (37.5)	458 (37.3)
	391 (71.2)	391 (71.0)
	350 (17.0)	351 (16.5)
Trans	588 (33.2)	588 (33.0)
	441 (29.0)	441 (28.8)
	418 (36.0)	418 (35.2)
	342.5 (13.3)	343 (13.5)

[a] Data on perchlorate salts with no added N(C$_2$H$_5$)$_4$Br; arbitrary temperature of 40°. [b] λ, nm; ε, M^{-1} cm^{-1}.

Table II. First-Order Rate Constants for the Reaction

$$cis\text{-Cr(en)}_2\text{Br}_2{}^+ \xrightarrow[\text{DMF}]{k_{12}} cis\text{-Cr(en)}_2\text{(DMF)Br}^{2+} + \text{Br}^-$$

T, °C	10^3[complex]$_0$, M	10^3[N(C$_2$H$_5$)$_4$Br]$_0$, M	10^5k_{12},[a] sec^{-1}
40.1	8.67	0	17.3,[b] 17.3[c]
40.3	8.88	0	18.3
40.1	8.83	0	16.9,[b] 16.7[d]
40.0	8.67	8.67	15.7
40.0	9.35	14.6	16.2
40.0	9.05	24.9	15.5
40.1	8.86	26.4	16.0
40.0	8.89	43.2	16.5
40.0	8.88	89.5	17.3
40.0	9.08	140.9	17.3
40.0	8.94	189.4	17.5
25.85	8.79	0	3.95
29.85	8.76	0	5.15,[b] 5.27[c]
36.25	8.27	0	11.0
36.9	8.79	0	14.3
37.0	8.76	0	15.5
37.1	8.79	0	15.8
40.5	8.71	0	18.8
45.0	8.68	0	27.2
45.55	8.80	0	33.7
45.6	9.43	0	32.5
50.5	8.79	0	59.3
55.0	8.80	0	78.7,[b] 78.2[c]
55.55	8.74	0	101.0
60.8	8.71	0	172.5
36.25	6.87	6.87[e]	10.5
40.0	10.17	18.6	16.3
45.7	5.01	5.01[e]	31.2
55.0	8.07	8.07[e]	70.7

[a] ±3%. [b] Calculated at 600 nm. [c] 620 nm. [d] 430 nm. [e] Runs conducted on *cis*-[Cr(en)$_2$]Br·H$_2$O in place of the usual perchlorate salt.

Results

1. *cis*- and *trans*-Cr(en)$_2$Br$_2$$^+$ in DMF. Figures 1 and 2 show the changes in visible absorption spectra which accompany the primary solvolysis of bromide ion (40°, no added bromide). Reactant and potential product pure absorption spectra are displayed in Figures 3 and 4 for each reaction. The observed isosbestic points (Table I, Figures 1 and 2) are indicative of simple stereoretentive solvolysis in each case. These points shift no earlier than 2$t_{1/2}$; new isosbestic points are established at a much later stage of reaction, consistent with the independently studied secondary reactions which will be reported elsewhere.[7] The positions (ε, λ) of the highest energy isosbestic points for primary solvolysis were observed to be slightly temperature and bromide dependent and this could be quantitatively accounted for in terms of the dependence of the component spectra on these variables in the "tail" of the charge-transfer region. We also found bromide dependence of the d–d spectrum of the *cis*-Cr(en)$_2$Br$_2$$^+$ ion in the lower energy region (*vide infra*). However, when due account was taken of these "medium" effects, the observed spectral changes were precisely those of simple stereoretentive solvolysis over the complete range of bromide (0–0.2 M) and temperature (25–60°) investigated. First-order rate constants were calculated in the usual ways from spectrophotometric data using the wavelengths closely corresponding to the observed isosbestic points for the secondary reaction. The wavelengths chosen varied somewhat with the conditions.[7] Good linear plots were obtained over 3$t_{1/2}$. The results are

Table III. First-Order Rate Constants for the Reaction

$$trans\text{-Cr(en)}_2\text{Br}_2^+ \xrightarrow[\text{DMF}]{k_{45}} trans\text{-Cr(en)}_2\text{(DMF)Br}^{2+} + \text{Br}^-$$

T, °C	10^3[complex]$_0$, M	10^3[N(C$_2$H$_5$)$_4$Br]$_0$, M	10^5k_{45},[a] sec^{-1}
40.15	12.3	0	12.8
40.05	8.63	17.3	13.5
40.20	9.19	26.9	12.8
40.10	8.63	34.7	12.8
40.20	9.28	43.3	13.3
40.20	10.16	89.2	14.0
34.80	25.1	0	6.5
39.65	18.4	0	10.8
42.8	14.5	0	15.5
51.2	29.6	0	37.7,[b] 37.7[c]
54.1	23.5	0	52.5
54.1	26.7	0	49.0
57.2	9.34	0	74.0
57.55	22.6	0	64.3
61.1	15.9	0	94.7
63.1	16.6	0	139.0
43.8	15.6	103.8	20.2
54.7	13.2	103.8	56.7

[a] ±3%. [b] Calculated at 550 nm. [c] Calculated at 560 nm.

Table IV. Summary of Kinetic Data for the Solvolyses

$$\text{Cr(en)}_2\text{Br}_2^+ \xrightarrow{\text{DMF}} \text{Cr(en)}_2\text{(DMF)Br}^{2+} + \text{Br}^-$$

Reactant complex	10^3[N(C$_2$H$_5$)$_4$Br]$_0$, M	10^5k (50°), sec^{-1}	$\Delta G^\ddagger$ (50°), kcal mol^{-1}	E_a, kcal mol^{-1}	$\Delta H^\ddagger$,[c] kcal mol^{-1}	$\Delta S^\ddagger$, cal mol^{-1} deg^{-1}
Cis	0	56.7	23.8	22.6	22.0	−5.5
	8.0[a]	51.7	23.9	22.6	22.0	−6.0
Trans	0	32.5	24.1	21.1	20.5	−11.0
	104[b]	36.5	24.0	20.1	19.5	−14.0

[a] [Complex]$_0$ = [N(C$_2$H$_5$)$_4$Br]$_0$ = 8 × 10^{-3} M. Complex approximately 60% ion paired. k_{12}(free ion) always 110–115% of k_{12}(ion pair) under the conditions investigated. [b] [Complex]$_0$ = 1.4 × 10^{-2} M. Complex significantly ion paired. [c] ±0.5 kcal mol^{-1}.

summarized in Tables II and III. Reproducibility was better than ±3% and we found no systematic dependence on [complex]$_0$ (no added bromide) or on wavelength used in the calculations, the latter observation confirming the assigned steric retention. The dependence of k_{12}(cis) and k_{45}(trans)[20] upon [N(C$_2$H$_5$)$_4$Br]$_0$ at a constant [complex] (8.8 × 10^{-3} M, cis; ~9 × 10^{-3} M, trans) and temperature (40°) is given in Tables II and III. Activation parameters derived from these data are given in Table IV.

2. *cis*- and *trans*-Cr(en)$_2$ClBr$^+$ in DMF and DMSO. The isosbestic point data given in Table V suggest that these solvolyses reactions proceed with a high degree of retention and, further, that bromide ion release is exclusive. The visible absorption spectra of the chloro(solvento) and potential product bromo(solvento) complexes were used in the stereochemical analyses; only the chloro(solvento) ions appear to be formed in both DMF and DMSO. This conclusion is supported by the consistency of the rate constants calculated at several wavelengths based on this assumption. Finally, potentiometric titration of partially reacted solutions (up to $2t_{1/2}$) left no doubt that >97% of the total halide initially released was bromide ion. Slow secondary reactions occur in these systems; some data have been published[3] on these and a fuller description will appear elsewhere.[7]

First-order rate constants (k_{12}^{Br} and k_{45}^{Br}) are given in Table VI together with a summary of results for related chromium(III) solvolyses. We have not investigated bromide ion or temperature dependence in the bromochloro systems.

Table V. Observed and Calculated Isosbestic Points for the Solvolysis Reactions in DMF and DMSO[a]

$$\text{Cr(en)}_2\text{ClBr}^+ \xrightarrow{\text{sol}} \text{Cr(en)}_2\text{(sol)Cl}^{2+} + \text{Br}^-$$

Reactant complex	Solvent	Isosbestic points λ (ε)[b] Obsd	Calcd for stereoretentivity
Cis	DMSO	347 (7.9)	347 (8.0)
		388 (66.5)	388 (66.0)
		463 (28.7)	463 (29.5)
		529 (85.9)	530 (86.2)
	DMF	348 (14.5)	347 (14.2)
		390 (68.0)	390 (67.9)
		456 (34.0)	455 (33.4)
		530 (82.5)	530 (81.8)
Trans	DMSO[c]	339 (6.1)	339 (6.5)
		411 (35.8)	412 (35.0)
		438 (27.0)	438 (26.6)
		573 (25.0)	574 (24.8)
	DMF[c]	409 (37.1)	410 (36.9)
		434 (26.4)	434 (26.4)
		573.5 (27.2)	574 (27.4)

[a] Data on perchlorate salts; temperature 40°. [b] λ, nm; ε, M^{-1} cm^{-1}. [c] Other isosbestic points are observed at early times (~450 and 500 nm), in essential agreement with those calculated, but are readily obscured by secondary reaction.

Table VI. First-Order Rate Constants for the Solvolysis of Dibromo, Dichloro, and Bromochloro Complexes in DMF and DMSO[a]

Reactant complex	Solvent	10^3[complex]$_0$, M	T, °C	10^5k_{Br}, sec^{-1}
cis-Cr(en)$_2$ClBr$^+$	DMF	11.1	49.3	37.3
	DMSO	7.53	49.55	56.7
trans-Cr(en)$_2$ClBr$^+$	DMF	14.4	49.3	20.3
	DMSO	12.6	49.55	41.8

Reactant complex	Solvent	10^5k_{X} (50°),[e] sec^{-1}	Solvent	10^5k_{X}(50°),[e] sec^{-1}
cis-Cr(en)$_2$Cl$_2^+$	DMF[c]	1.17	DMSO[c]	2.55
trans-Cr(en)$_2$Cl$_2^+$	DMF[c]	0.35	DMSO[c]	0.75[b]
	DMSO[c]	0.18	DMSO[c]	1.57[f]
cis-Cr(en)$_2$Br$_2^+$	DMF[d]	28.3	DMSO[c]	45.7
trans-Cr(en)$_2$Br$_2^+$	DMF[d]	16.3	DMSO[c]	40.7

[a] [Added X$^-$]$_0$ = 0, except where noted. [b] Data for Cl$^-$ exchange; plot of k_{ex} *vs.* [Cl$^-$]$_0$ extrapolated to [Cl$^-$]$_0$ = 0. [c] Data from ref 1, 2, and 4. [d] This work. [e] Corrected for statistical factor of 2. [f] Cl$^-$ exchange; [Cl$^-$]$_0$ = 36.8 × 10^{-3} M.

3. Equilibria. Primary solvolysis is complete under all conditions in the dibromo system. Only the *cis*-Cr(en)$_2$(DMF)Br^{2+} and *cis*-Cr(en)$_2$(DMF)$_2^{3+}$ complexes are present at equilibrium even at high concentrations of added bromide ion ([complex]$_0$ = (6.5–8.8) × 10^{-3} M, [N(C$_2$H$_5$)$_4$Br]$_0$ = 0–0.2 M).[7] Primary solvolysis is also significant (>90%) but measurably incomplete for both the *cis*- and *trans*-bromochloro cations in DMF and DMSO. We have not investigated the equilibria in the latter systems over a range of bromide due to complications, one of which is bromide anation of bound chloride. However, our observation of incomplete solvolysis has been confirmed by observing the back-reaction, *i.e.*, the slight but significant replacement of complexed solvent in *cis*-Cr(en)$_2$(sol)Cl^{2+} by bromide ion in DMF and DMSO. Primary solvolysis of the bromochloro isomers is marginally more extensive in DMSO (at 50°, [complex]$_0$ = 10 × 10^{-3} M and [total bromide]$_0$ = 20 × 10^{-3} M). This reversibility did not seriously interfere in rate constant calculations.

Discussion

Stereochemistry. The solvolyses reported here are strictly retentive like their aquation reactions[6,16] and this is typical of octahedral chromium(III) substitution of tetraamine complexes in the absence of chromium–nitrogen bond rupture. The stereochemistry of the analogous cobalt(III) reactions is not known since the *trans*-halo(solvento) isomers, if formed,

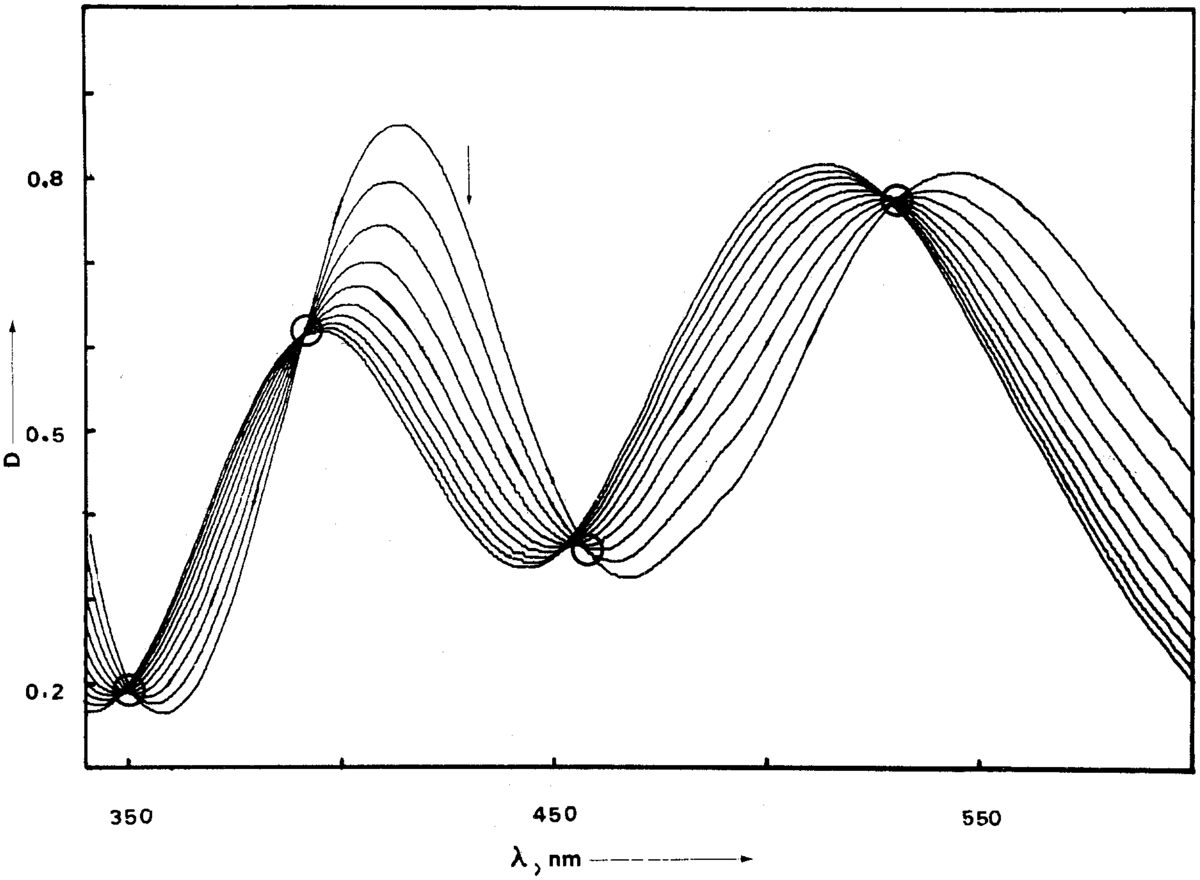

Figure 1. Reaction of *cis*-$Cr(en)_2Br_2^+(ClO_4^-)$ in DMF. Spectral scans cover a period of approximately 3 half-lives; $[N(C_2H_5)_4Br]_0 = 0$; $T = 40°$.

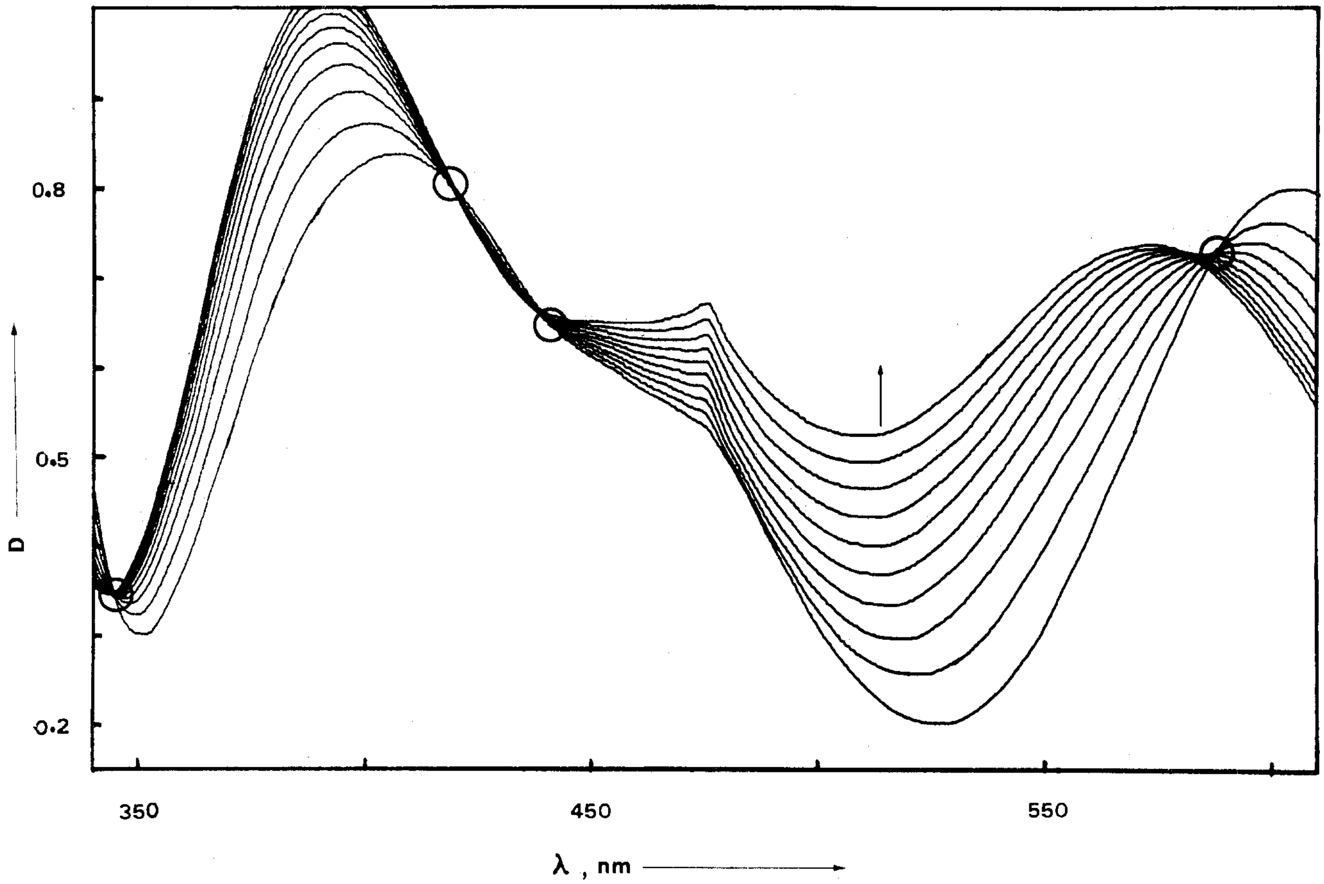

Figure 2. Solvolysis of *trans*-$Cr(en)_2Br_2^+$ in DMF. Changes in absorption spectra cover a period of approximately 2 half-lives; $[N(C_2H_5)_4Br]_0 = 0$; $T = 40°$.

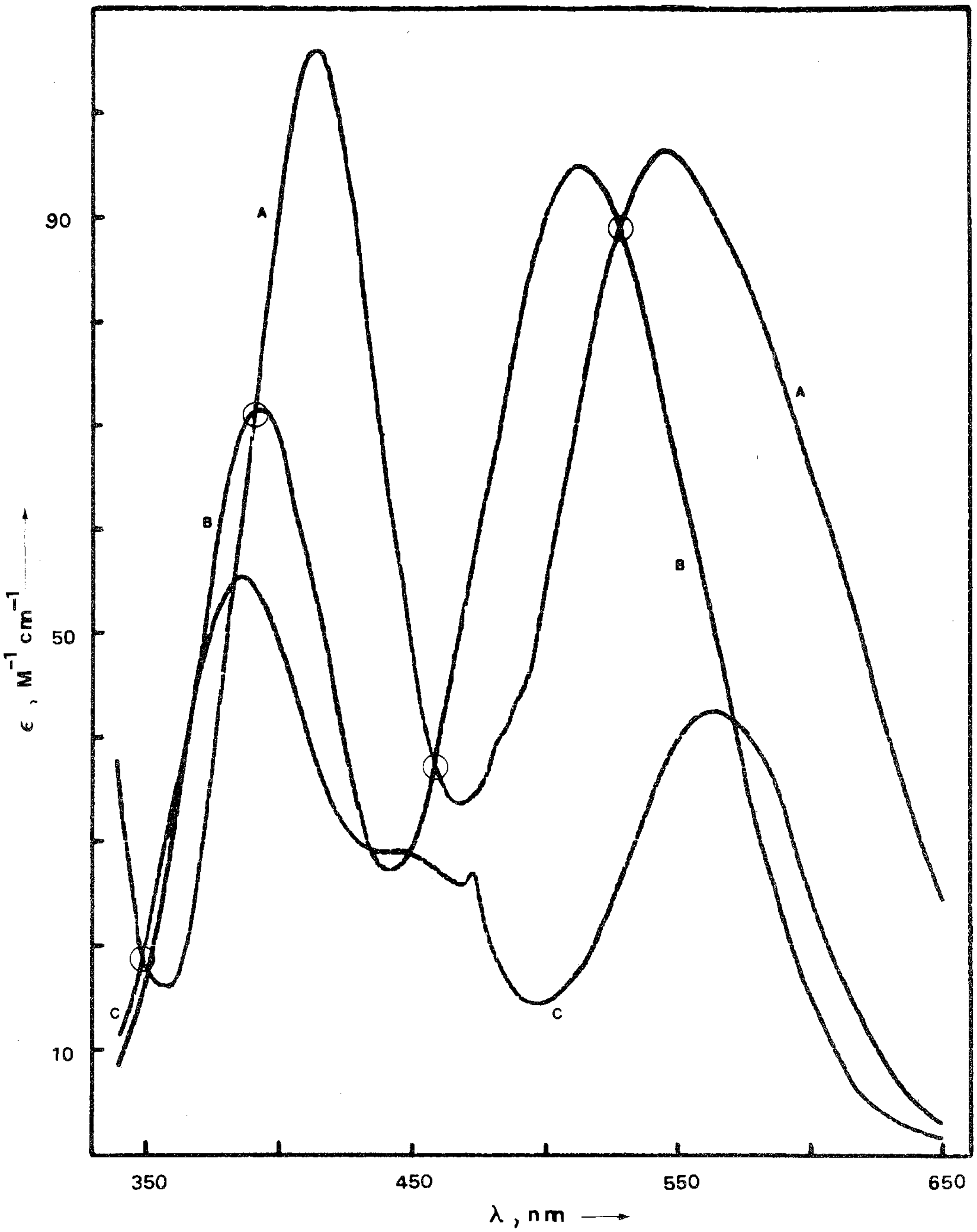

Figure 3. Pure absorption spectra in DMF at 25°: A, *cis*-$Cr(en)_2Br_2^+(ClO_4^-)$; B, *cis*-$Cr(en)_2(DMF)Br^{2+}$; C, *trans*-$Cr(en)_2(DMF)Br^{2+}$.

rapidly isomerize to the cis form and escape detection.[21] It does seem likely, however, that some direct stereochemical change does occur with Co(III) as it does with the analogous aquation reactions.

Equilibria. In DMSO and DMF, solvolysis in both chloro and bromo chromium(III) systems is more extensive than in their cobalt(III) analogs.[1-5,7,22] Oxygen-bonded solvent ligands appear to form stronger complexes with chromium(III). There is ample support for this view.[23,24] This effect is particularly marked for the bromochromium(III) systems; this suggests further that the metal–bromide bond is weaker for chromium than for cobalt. This idea is supported by bonding parameters deduced from spectra[24] and is consistent with the kinetic results discussed ahead. The greater solvolysis in DMSO (over DMF) observed here and elsewhere[22] for both cobalt(III)– and chromium(III)–halo complexes may reflect the stronger metal–DMSO bond,[7,21,25] or it may simply reflect the net effect of differential cation and anion solvation. It should be noted that anion solvation (Br^- stronger than Cl^-) is weak in these solvents[22] and normally is not a dominant factor in determining *relative* equilibrium positions (*e.g.*, bromo *vs.* analogous chloro complex in the same solvent), although clearly this factor is responsible for the common observation of solvolytic reversibility in dipolar aprotic media when compared with analogous aqueous systems.

Ion Association. Ion pairing of the dibromo complexes with bromide ion has been shown to be significant in DMF,[5] although the anticipated effects are not clearly evident in the kinetics (Tables II and III). We have observed quite generally that the carefully measured d–d spectra of *cis*-dihalotetraaminechromium(III) cations depend upon the concentration of added halide ion in dipolar aprotic media. Ion pairing has not previously been reported measurably to affect purely d–d spectra. This effect is not unlike the usual solvent dependence of spectra, but the significant observation is that the spectra of the *trans*-dihalo and *cis*- and *trans*-solvento complexes, in

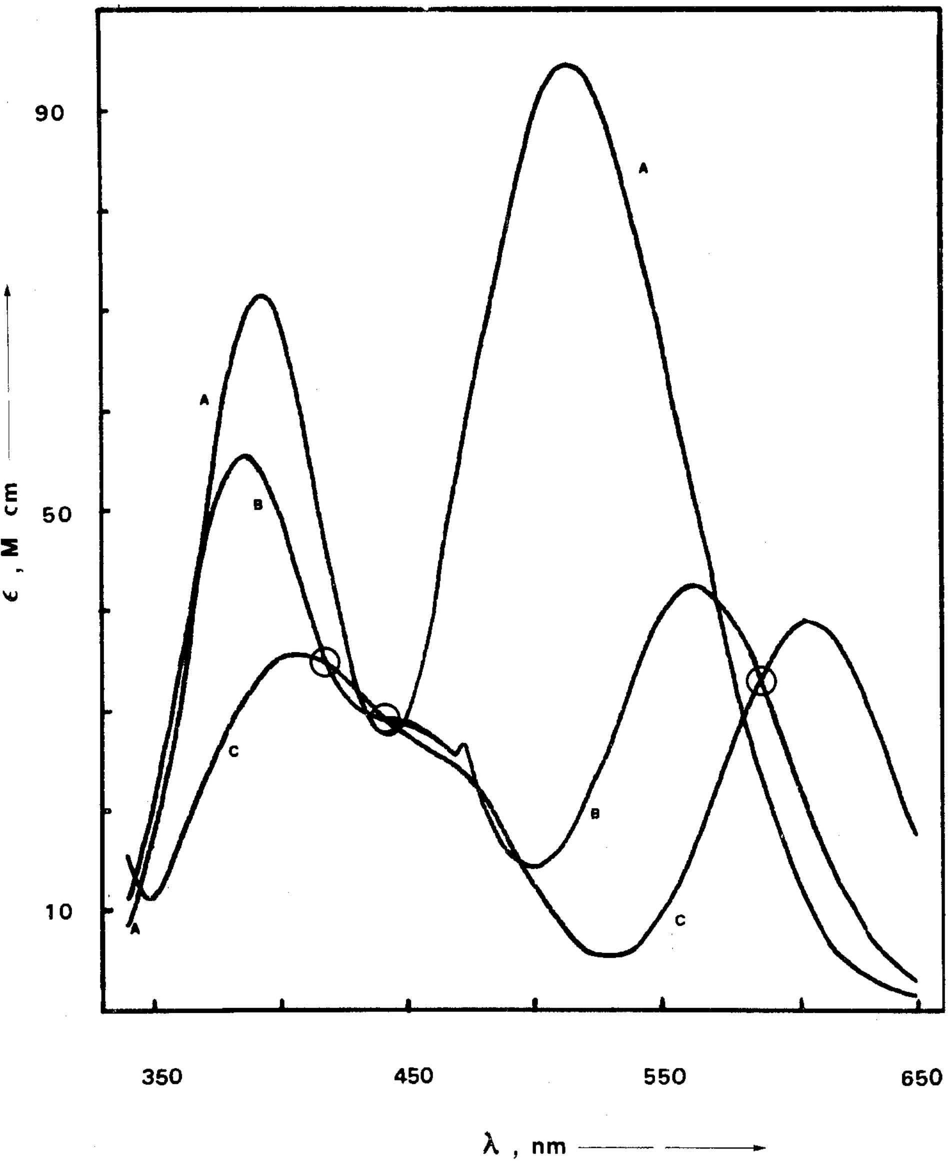

Figure 4. Pure absorption spectra in DMF at 25°: A, *cis*-$Cr(en)_2(DMF)Br^{2+}$; B, *trans*-$Cr(en)_2(DMF)Br^{2+}$; C, *trans*-$Cr(en)_2Br_2^+$.

contrast, show no detectable halide ion dependence even under conditions of significant ion association, whereas they do show a not unexpected solvent dependence. Previous work[5] has suggested that *cis*- but not *trans*-dihalo complexes form ion pairs in which the counteranion is specifically located in the secondary coordination sphere, away from the repulsive complexed halide ions and hydrogen bonded to the amine ligands. This idea is almost certainly related to the aforementioned d–d spectral effects which curiously are also specific for *cis*-dihalo complexes.

In the case of *cis*-$Cr(en)_2Br_2^+$ with Br^- in DMF, the maximum changes in ε are significant although small (10–20%), the lower energy T_{2g} manifold being the more affected. Attributing the ε changes to ion pairing, we obtained a value for the ion-pair constant (k_{IP}) of ~500 M^{-1} (20°), in reasonable agreement with that determined by precise conductometric measurements[5] (K_{IP} = 913 M^{-1}, 25°); the discrepancy is readily reconciled with the errors in our estimation. Solvent absorption prevented a more accurate K_{IP} determination through the more usual spectrophotometric method of monitoring uv absorption where ε changes are greater.

Kinetics. It is apparent that the free ion and ion pair have an almost identical reactivity for both the *cis*- and *trans*-$Cr(en)_2Br_2^+$ solvolyses in DMF (Tables II and III). Clearly significant ion pairing occurs under our conditions but it must be emphasized that the rate profiles represent a compromise between the pronounced "medium" effects of both the ground and transition states, in the form of ion association and bromide ion–solvent competition at the transition state (or in a reduced coordination number intermediate). Even if significant mass law retardation were possible, the effects of ion association may well be dominant. Thus the observed solvolysis rate of the ion pair may be more than, equal to, or less than that of the free ion for, say, an I_d or D process, as stressed previously,[22] and thus such rate profiles are generally not mechanistically discriminating. Cases of very similar free-ion and ion-pair reactivity as observed here are more usually found in reactions involving both neutral incoming and leaving groups.[4]

The solvolysis rates of the present and related reactions (Table VI) are considered further as follows: (i) the relative rates of bromide and chloride release, (ii) cis:trans reactivity ratio, and (iii) the effect of solvent transfer on these rate ratios. Commonly bromide is released faster than chloride and we note that the Br:Cl rate ratio is 25–30 in the chromium systems in DMF and DMSO (*e.g.*, when comparing the *cis*-dibromo with the corresponding *cis*-dichloro complex in the same solvent). Thus it is not surprising to see exclusive bromide solvolysis in both the bromochloro isomers ($k_{Br}/k_{Cl} > 30$). In analogous cobalt(III) systems[22] this ratio is considerably smaller (5–10) in these solvents. Bromide and chloride are released together from the bromochlorocobalt(III) isomers in DMSO (unreported proportions[10]) but there is predominance of bromide solvolysis for the same complexes in DMF.[10] The weaker metal–bromide bond for both Cr(III) and Co(III) and, to a lesser degree, the established order of the weak anion solvation in these solvents ($Br^- > Cl^-$) neatly accommodate these observations if halide dissociation is well advanced at the first transition state (d activation[26]). The higher Br:Cl ratio in the case of chromium is consistent with the greater difference in metal–chloride and metal–bromide bond strengths and, in particular, suggests weak chromium–bromide bonding, an idea which was advanced earlier in connection with equilibrium results.

It is noteworthy that the Br:Cl rate ratio is significantly smaller in water than in DMF or DMSO (typically ~10 for chromium and ~5 for cobalt), consistent with the reversal in the order and increased importance of anion solvation in water ($Cl^- > Br^-$); again, these observations support the idea of an essentially dissociative process for the solvolyses of both metal complexes in water and dipolar aprotic media.

A cis isomer commonly aquates more rapidly than its trans form (by a factor of ~5–10),[27] and it may be noted that the effect of changing the solvent to DMF or DMSO is to diminish this reactivity ratio in both chromium(III) (Table VI) and cobalt(III) systems. Indeed, rates of cis and trans solvolysis are almost the same; for cobalt(III),[8-12,22] the trans isomer is frequently the slightly more reactive isomer in DMF and DMSO. For an apparent exception (*cis*- and *trans*-$Cr(en)_2Cl_2^+$ in DMSO[2,3]) there is a significant retentive chloride-exchange path for the trans form and hence the measured solvolysis rate is less than the true dissociation rate. The ground-state stabilization of the dipolar *cis*-dihalo cation relative to the trans form has been many times demonstrated in dipolar aprotic media,[22] and this factor alone is sufficient to account for the aforementioned observation but we again emphasize that transition state solvation is equally as important as that which can be attributed to the ground state. However the trans isomer that has no or only a small permanent ground-state dipole moment (*e.g.*, *trans*-$Cr(en)_2Br_2^+$ and *trans*-$Cr(en)_2ClBr^+$) will gain more than the cis isomer in cation solvation through developing a 2+ dipolar transition state in dissociative (d) solvolysis; thus increased relative trans:cis lability on solvent transfer from water to these dipolar aprotic solvents is expected for d activation and indeed it is observed. Langford[25] has argued, by analogy with observations on organic halides, that the "absolute" rate of solvolysis of a halo inorganic complex is diminished because of the greatly reduced contribution of leaving group solvation to the solvolysis rate. We emphasize here that it is the solvolysis rate of the cis isomer that is consistently more reduced than that of the trans form on solvent transfer (water to DMF or DMSO). Both observations support a dissociative mechanism.

We make one final comment, namely, that in both cobalt(III) and chromium(III) systems, DMSO solvolysis is consistently faster (by a factor of ~2) than for DMF; any reasonable explanation of this result must remain equivocal.

There is increasing evidence to support the suggestion that at least for certain classes of chromium(III) complex reactions, the intimate mechanism[26] is I_a.[28,29] The consequences of "a" activation are not easily realized in solvolysis reactions involving anionic leaving groups but the rationale presented strongly suggests that the Cr(III) reactions are essentially dissociative, as their Co(III) analogs undoubtedly are.

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Registry No. *cis*-$Cr(en)_2ClBr^+$, 45838-11-7; *trans*-$Cr(en)_2ClBr^+$, 29844-98-2; *cis*-$Cr(en)_2Cl_2^+$, 14482-74-7; *trans*-$Cr(en)_2Cl_2^+$, 14403-88-4; *cis*-$Cr(en)_2Br_2^+$, 20631-53-2; *trans*-$Cr(en)_2Br_2^+$, 33882-25-6; *cis*-$Cr(en)_2(DMF)Br^{2+}$, 46361-63-1; *trans*-$Cr(en)_2(DMF)Br^{2+}$, 46361-62-0; *cis*-$Cr(en)_2(DMSO)Cl^{2+}$, 46240-37-3; *cis*-$Cr(en)_2(DMF)Cl^{2+}$, 19066-42-3; *trans*-$Cr(en)_2(DMSO)Cl^{2+}$, 29844-97-1; *trans*-$Cr(en)_2(DMF)Cl^{2+}$, 46361-64-2.

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