Solvent Interchange Studies on Octahedral Bis(ethylenediamine) and Tetra-amminechromium(III) Complexes

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The kinetics of the following sixteen reactions have been investigated: cis-$CrN_4(sol_1)Cl^{2+}$–SOL_2 → cis-$CrN_4(sol_2)Cl^{2+}$ + SOL_1; $N = NH_3$, ½ en; sol_1 = OH_2, dmf, dma; SOL_2 = DMSO; cis-$Cr(en)_2(sol_1)_2^{3+}$–SOL_2 → cis-$Cr(en)_2(sol_2)_2^{3+}$ + $2SOL_1$; sol_1 = dmf, dma; SOL_2 = DMSO; sol_1 = dmso; SOL_2 = DMF; sol_1 = dma, dmso; SOL_2 = H_2O. The intermediate cis-$Cr(en)_2(sol_1)(sol_2)^{3+}$ species have been isolated and separately investigated. For cis-$Cr(NH_3)_4(OH_2)$-Cl^{2+}, Cl^- and NH_3 loss sidereaction in DMSO occurs via the labile deprotonated (hydroxo) complex, a path suppressed with $HClO_4$. Further studies [9] on the much less reactive trans isomers show isomerization the dominant path with some parallel amine loss. They are shown to play no role in the reactions of the cis isomers which proceed with strict stereoretention. Reactivity patterns for neutral leaving groups are discussed in detail. The cis solvent interchange rates are seen to approximate the exchange rates. The significant cis >> trans reactivity order is explained in terms of a specific trans-N labilization and is supported by other data. Equilibrium data are presented; Cl^- and amine release have been followed and an indicator method for the quantitative estimation of the latter is detailed. Activation parameters are reported for most reactions and the mechanisms are discussed.

Introduction

Among the criteria used to assess the mechanism of octahedral substitution are the effects of steric crowding, charge, chelation, solvent, electron displacement, and the stereochemistry of substitution. The rationalization of these effects, however, cannot be achieved without a certain degree of equivocation. The problem relates to the difficulty in varying just the one influence (*e.g.*, leaving group) within a series of closely related complexes. An experiment that may bear informatively on this point is one where both the entering and leaving groups are electrically neutral. Electrorestrictive effects are expected to be absent as there is no formal charge redistribution [2a, 3].

Information connected with this type of process for the inert metal complexes (*e.g.*, Co(III) and Cr-(III)) is scattered. Solvent exchange studies which have furnished the bulk of this data usually have been conducted in conjunction with isomerization, racemization [4] and anation [5] experiments, and few attempts have been made to analyse the reactivity patterns of solvent exchange in their own right.

Watts *et al.* [6–8] have reported a series of reactions closely related to solvent exchange: cis-Co(en)$_2$-(sol$_1$)Cl^{2+} + SOL$_2$ → cis-Co(en)$_2$(sol$_2$)Cl^{2+} + SOL$_1$. These solvents include water [6], dimethylformamide (dmf), dimethylacetamide (dma) and dimethylsulphoxide (dmso) [7, 8]. In this work we describe a related and wider series of reactions for bis(ethylenediamine) and tetra-amminechromium(III) complexes. Critically examined are the rates and steric course of substitution, and the effects of solvent, charge and chelation, factors more easily assessed in the absence of electrorestriction. The present work is confined mainly to cis complexes where the reaction is simply solvent interchange; the *trans* isomers which lose amine and isomerize in parallel reactions are considered in more detail elsewhere [9].

Experimental

Complexes

All the Cr(en)$_2$ solvento complexes were prepared by essentially the same technique, retentive Ag$^+$ promoted solvolysis of halo complex in the appropriate solvent [10]. Typical procedure follows.

Cis-Cr(en)$_2$(sol)Cl^{2+} (sol = dmf, dma, dmso) were prepared from cis-[Cr(en)$_2$Cl$_2$]ClO$_4$ [10] (14.0 mmol) and a stoichiometric excess of AgClO$_4$*

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*AgNO$_3$ is unsatisfactory and leads to significant NO$_3^-$ coordination.

14.7 mmol; 1.05 equiv) in SOL (2×20 ml, 60 °C, 10 min). The cooled product solution was freed of AgCl by the addition of acetone (50 ml) and fine porosity sintered glass filtration. Pouring into ether (300 ml) or ethanol/ether (1:4, 500 ml) produced an oil which after decantation was extracted with ethanol and ether to remove excess solvent. The oil in a minimum volume of cold water (5 °C, ~10 ml) was set aside for 5 min*, treated with a trace of $Na_2S_2O_3$ and saturated aqueous $NaClO_4$ (3g, 5 ml)**, and quickly filtered. The well-formed crystals which deposited on standing (0 °C, 1–2 hr) were collected, washed with ethanol and ether, and air-dried. Seeding or vigorous scratching was occasionally required to initiate crystallization because of the common tendency to supersaturation. One or two recrystallizations from water afforded the pure complex, typically in 80–90% overall yield.

The appropriate alterations to the conditions for the other solvento complexes are noted below in parenthesis. 1.05 or 2.10 equiv of $AgClO_4$ were used. cis-$Cr(en)_2(sol)_2^{3+}$ (sol = dmf, dma, dmso) were synthesized from cis-$[Cr(en)_2(sol)Cl](ClO_4)_2$ (60 °C, 10 min), cis-$[Cr(en)_2(sol)Br](ClO_4)_2$ (60 °C, 1 min) (*vide infra*), cis-$[Cr(en)_2Cl_2]ClO_4$ [9] (60 °C, 15 min), or more usually cis-$[Cr(en)_2Br_2]ClO_4$ [11] (60 °C, 2 min; 20 °C, 20 min). Yields of these and others described briefly below were again in the range 80–90%.

Cis-$[Cr(en)_2(sol)Br](ClO_4)_2$ (sol = dmf, dma, dmso) were generated from cis-$[Cr(en)_2Br_2]ClO_4$ (20 °C, 30 min).

$Trans$-$Cr(en)_2(sol)_2^{3+}$ (sol = dmf, dma, dmso) were prepared from $trans$-$[Cr(en)_2(sol)Br](ClO_4)_2$ or $trans$-$[Cr(en)_2Br_2]ClO_4$ [9] 20 °C, 60–120 min).

$Trans$-$[Cr(en)_2(dmso)Br](ClO_4)_2$ was prepared from $trans$-$[Cr(en)_2Br_2]ClO_4$ (20 °C, 60 min).

$Trans$-$[Cr(en)_2(sol)Cl](ClO_4)_2$ (sol = dmf, dmso) preparations employed $trans$-$[Cr(en)_2ClBr]ClO_4$ [10] or better $trans$-$[Cr(en)_2ClI]ClO_4$ [10] as starting material (20 °C, 60 or 20 min, respectively). $Trans$-$[Cr(en)_2Cl_2]ClO_4$ is unsatisfactory.

$Trans$-$[Cr(en)_2(dmso)(ONO)](ClO_4)_2$ was prepared from $trans$-$[Cr(en)_2Br(ONO)]ClO_4$ [10] (20 °C, 60 min); the latter was obtained through the sequence $trans$-$[Cr(en)_2Br_2] Br \cdot H_2O-H_2O,H^+ \longrightarrow trans$-$Cr(en)_2(OH_2)Br^{2+}-NO^+ \longrightarrow trans$-$Cr(en)_2Br(ONO)^+$.***

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*This procedure removes any residual reactant through the more rapid Ag^+ promoted aquation. The more soluble aquo complex remains in solution.

**To obtain the nitrate perchlorate, $NaNO_3$ (2g, ~10 ml H_2O) was also added.

***A significant typographical error occurs in ref. 10; $NaClO_4$ is added and unreacted $trans$-$[Cr(en)_2Br_2]ClO_4$ is removed by filtration *before* the addition of $NaNO_2$.

To authenticate the mixed solvento species cis- and $trans$-$Cr(en)_2(dmf)(dmso)^{3+}$ and cis-$Cr(en)_2$-$(dma)(dmso)^{3+}$, two distinct routes were followed: $[Cr(en)_2(sol_1)Br](ClO_4)_2$ in SOL_2, and $[Cr(en)_2$-$(sol_2)Br](ClO_4)_2$ in SOL_1 (5 equiv $AgClO_4$). The specific conditions are important if contamination with the *bis*(solvento) species is to be entirely avoided: cis, sol_1 = dmf, dma, SOL_2 = DMSO, 20 °C, 10 min; sol_1 = dmso, SOL_2 = DMF, DMA, 20 °C, 35 min; $trans$, sol_1 = dmf, SOL_2 = DMSO, 20 °C, 30 min; sol_1 = dmso, SOL_2 = DMF, 20 °C, 60 min. The chloro solvento complexes are not suitable reactants; solvent interchange becomes comparable in rate to Ag^+ promoted Cl^- loss and leads to a significant *bis*-(solvento) impurity.

$Trans$-$[Cr(en)_2(dmso)(OH_2)](ClO_4)_3$

A thin paste of $trans$-$[Cr(en)_2(dmso)ONO)]$-$(ClO_4)_2$ (3.0 g) in $HClO_4$ (40%) was stirred for 15 min at 0 °C. The resultant violet slurry in acetone (0 °C, 30 ml) was filtered and ether added slowly to precipitate the product. Reprecipitation from acidified acetone with ether afforded crystals of pure complex in ~90% yield.

Cis-$[Cr(en)_2(OH_2)OH]S_2O_6 \cdot H_2O$ [12] was purified by dropwise addition of pyridine to a filtered solution in $HClO_4$ (0.05 M, 0 °C).

$Trans$-$[Cr(en)_2(OH_2)_2]Br_3$

$Trans$-$[Cr(en)_2Br_2] Br$ (4.0 g, 0.9 mmol) in water (50 ml) containing HBr (48%, 0.5 ml) was allowed to aquate in the dark (4 hr, 25 °C). Rapid $trans$-$Cr(en)_2$-$(OH)Br^+$ aquation by the addition of pyridine (5 ml) afforded a deep violet solution (3 min) from which lustrous orange crystals separated on reprotonation with HBr (48%, 30 ml) and cooling. The complex was recyrstallized from cold water by the additon of HBr (48%). Yield ~70%. The addition of NaBr or $NaClO_4$ followed by pyridine to aqueous solutions of the diaquo complex yielded the respective salts of the less soluble and pure $trans$-$Cr(en)_2(OH_2)OH^{2+}$ complex.

Cis-$[Cr(en)_2(OH_2)Cl] Br_2 \cdot H_2O$ [13] was purified by adding a filtered saturated methanol solution to a twentyfold volume of *iso*-propanol. $Trans$-$[Cr(en)_2$-$(OH_2)Cl] Br_2$ and $trans$-$[Cr(en)_2(OH_2)Cl] (ClO_4)_2 \cdot 0.5 H_2O$ were prepared and purified as described previously [10].

Recrystallized cis-$[Cr(NH_3)_4(OH_2)Cl] (ClO_4)_2$ [14, 15] was converted to the bromide by the addition of HBr (48%) to an ice-cold aqueous solution. $Trans$-Cr-$(NH_3)_4(OH_2)Cl^{2+}$ was obtained as the chloride, bromide and perchlorate salts [14, 15]. It was convenient to initially purify the complex *via trans*-$[Cr(NH_3)_4(ONO)Cl] ClO_4$ [17], as described for the bromo analogue [16].

Cis-[Cr(NH₃)₄(sol)Cl](ClO₄)₂ (sol = dmf, dma, dmso)

Cis-$Cr(NH_3)_4(OH_2)Cl$ $(ClO_4)_2$ (4.0 g, 10.6 mmol) in SOL (50 ml) containing $HClO_4$ ($3M$, 0.5 ml) was allowed to react thus: SOL = DMSO (3.5 hr, 45 °C), DMA (100 min, 45 °C) or DMF (90 hr, 18 °C). The work up essentially followed that described for the $Cr(en)_2$ analogues, except that cis-$[Cr(NH_3)_4(dma)$-$Cl](ClO_4)_2$ which gave gelatinous crystals from water decomposed quickly when pumped dry on the filter. Here the recrystallized material was kept moist with the last ether washing during transfer to a desiccator. Note that although these complexes may also be prepared from cis-$[Cr(NH_3)_4Cl_2]ClO_4$ [43] by the analogous *bis*(ethylenediamine) procedure, the starting material is less readily available than the aquochloro complex.

Trans-$[Cr(NH_3)_4(dmso)Cl](ClO_4)_2$ was prepared from $trans$-$[Cr(NH_3)_4ClBr]ClO_4$ in DMSO (1.05 equiv $AgClO_4$, 20 °C, 35 min).

Cis-$[Cr(NH_3)_4(dmso)_2](ClO_4)_3$ was prepared from cis-$[Cr(NH_3)_4(dmso)Cl](ClO_4)_2$ according to the bis(ethylenediamine) procedure (DMSO, 3 equiv $AgClO_4$, 50 °C, 90 min). Cold *iso*-propanol was used to initially precipitate the oil. Recrystallization from water (twice, $NaClO_4$) afforded bright orange platelets.

$Cr(en)(OH_2)_4^{3+}$ was prepared in 3M $HClO_4$ solution [18]. A constant spectrum was assured by repeated chromotography (Dowex 50W X 2, 200–400 mesh, H^+ form, $3M$ $HClO_4$ final eluant).

[Hg(dmso)₆](ClO₄)₂

Purified HgO [19] in excess $HClO_4$ (40%) was diluted carefully with a tenfold volume of DMSO. Triethylorthoformate was added and the mixture warmed (60 °C, 10 min). The slow addition of excess alcohol and ether yielded colorless crystals. Recrystallization from DMSO afforded the pure solvate which was transferred to a desiccator while still wet with ether to mininize aerial hydrolysis.

Characterization

Analytical data (Table I) were satisfactory. Isomeric purity was established according to previously recorded criteria [20, 21]. For new complexes the distinction between *cis* and *trans* isomers is based on electronic spectra and comparison between $Cr(en)_2$ and $Cr(NH_3)_4$ analogues. Assignments are unambiguous since *cis/trans* pairs are known in all cases and the differences are clear [22]. The potentially ambient ligands dmf, dmso, and dma are O-bound on the basis of the close similarity in electronic spectra to their aquo counterparts. In the ir spectra (Table II) the shifts to lower frequencies in S–O (dmso) and C–O vibrations (dmf, dma), and increases in the O–C–N deformation bands (dmf, dma, upon solvent co-ordination are further diagnostic of O-bonding [23].

Except for solvates, complexes were stored *in vacuo* in the dark over P_2O_5. Fresh preparations were generally employed because of a tendency to slow dark decomposition (particularly $trans$-$Cr(en)_2$-$(dmso)(OH_2)](ClO_4)_3$).

Media

Acid solutions were prepared from doubly distilled water and Analar $HClO_4$ standardized against HgO. Ionic strength was adjusted with Analar $NaClO_4 \cdot H_2O$ or $NaNO_3$. Purified HgO [19] in $HClO_4$ or HNO_3 ($2M$) provided Hg_{aq}^{2+}. $AgClO_4$ was prepared from Ag_2-CO_3 and $HClO_4$. DMSO, DMF, and DMA were dried and purified as reported [24] and were freshly (doubly) distilled for immediate use.

Instruments

All electronic spectra were measured on either a Hitachi EPS-3T or Unicam SP800 self-recording spectrophotometers. No significant ($\epsilon_\lambda < \pm 1\%$) temperature dependence was noted (0–60 °C). Ir spectra of powdered samples pressed in KBr discs were measured on Perkin–Elmer model 421 and 457 instruments.

Kinetics

(i) Reactions followed spectrophotometrically employed both the *in situ* technique [16, 20] and for slower runs, a sampling method [9]. Temperature control (±0.1 °C) and measurement followed earlier directions [16, 20]. Repetitive scanning (340–700 nm) was used to follow all reactions; absorbance–time scanning at suitable fixed wavelengths was employed to collect the bulk of the rate data. Light was excluded from all runs. Perchlorate salts were used except where noted otherwise.

(ii) Cl^- release from cis-$CrN_4(sol)Cl^{2+}$ in DMSO. A sampling technique was used. Aliquots (10.00 ml), cooled to 15 °C, were quenched with ice-cold $HClO_4$ (0.05 M, 15 ml) and the mixture sorbed onto a jacketed (0 °C) column (60 X 10 mm) of Dowex AG50W-X8 cation exchange resin (H^+ form, 100–200 mesh). Free Cl^- was rinsed quickly (pressure) form the resin with ice-cold $HClO_4$ (0.05 M). The collected effluent was analysed for Cl^- by standard potentiometric methods (Ag/AgCl electrode). A freshly prepared and unheated solution of each complex was treated similarly; liberated Cl^- served as a blank.

(iii) NH_3 release from *cis*- and $trans$-$Cr(NH_3)_4$-$(dmso)Cl^{2+}$ in DMSO. A sampling method was again employed. Successive 2.00 ml aliquots of the reaction mixture (*ca.* 10^{-4} M in Cr) were cooled (~22 °C) and the absorbance measured after the addition of 3-phenyl-2-benzofuranone (PBF, *ca.* 4 mg). The NH_3 concentration was calculated for ϵ_{353}^{max} for PBF or read directly from a calibration graph. A sample of DMSO

TABLE I. Analytical Data for Some Chromium(III) Complexes[a].

Complex		Cr	C	H	N	Cl	Br	S
cis-[Cr(en)$_2$(OH$_2$)Cl] Br$_2$·H$_2$O	F		12.1	5.0	14.0	8.9	39.1	
	C		11.9	5.0	13.9	8.8	39.6	
trans-[Cr(en)$_2$(OH$_2$)Cl] Br$_2$	F	13.5	12.1	5.0	14.4	9.3	41.4	
	C	13.5	12.4	4.7	14.5	9.2	41.5	
trans-[Cr(en)$_2$(OH$_2$)Cl] (ClO$_4$)$_2$·0.5H$_2$O	F	12.0	11.1	4.7	12.5	24.7		
	C	12.0	11.1	4.4	12.9	24.5		
trans-[Cr(en)$_2$(OH$_2$)$_2$] Br$_3$	F	11.4	10.7	4.5	14.1		53.0	
	C	11.4	10.5	4.4	14.0		52.6	
trans-[Cr(en)$_2$(OH$_2$)(OH)] (ClO$_4$)$_2$	F		12.0	4.8	14.0	17.3		
	C		11.9	4.7	13.8	17.3		
trans-[Cr(en)$_2$(OH$_2$)(OH)] Br$_2$	F		13.0	5.2	15.2		43.7	
	C		13.1	5.2	15.3		43.5	
cis-[Cr(en)$_2$(OH$_2$)(OH)] S$_2$O$_6$·H$_2$O	F		12.6	5.3	14.6			16.8
	C		12.5	5.5	14.5			16.6
trans-[Cr(en)$_2$(dmso)(OH$_2$)] (ClO$_4$)$_3$	F		12.5	4.3	10.0	18.9		5.6
	C		12.7	4.3	9.9	18.8		5.7
cis-[Cr(en)$_2$(dmf)Cl] (ClO$_4$)$_2$	F	10.6	17.8	4.9	14.4	22.6		
	C	10.8	17.5	4.8	14.6	22.2		
trans-[Cr(en)$_2$(dmf)Cl] (ClO$_4$)$_2$	F		17.4	4.9	14.4	22.2		
cis-[Cr(en)$_2$(dmso)Cl] ClO$_4$NO$_3$	F		16.0	4.9	15.7	15.8		6.9
	C		16.1	5.0	15.7	15.9		7.2
trans-[Cr(en)$_2$(dmso)Cl] (ClO$_4$)$_2$	F		14.9	4.6	11.3	21.9		6.5
	C		14.9	4.5	11.5	22.0		6.6
cis-[Cr(en)$_2$(dma)Cl] (ClO$_4$)$_2$	F	10.8	19.6	5.1	13.9	21.4		
	C	10.5	19.5	5.1	14.2	21.6		
cis-[Cr(en)$_2$(dmf)Br] (ClO$_4$)$_2$	F		16.1	4.6	13.3	13.5	15.2	
	C		16.1	4.4	13.4	13.5	15.3	
cis-[Cr(en)$_2$(dmso)Br] (ClO$_4$)$_2$	F	9.9	13.8	4.2	10.4	13.2	15.1	6.0
trans-[Cr(en)$_2$(dmso)Br] (ClO$_4$)$_2$	F		13.6	4.2	10.6	13.5	15.3	
	C	9.8	13.6	4.2	10.6	13.4	15.1	6.1
cis-[Cr(en)$_2$(dma)Br] (ClO$_4$)$_2$	F	9.5	18.1	4.8	12.8	13.4	15.2	
	C	9.6	17.9	4.7	13.0	13.2	14.9	
cis-[Cr(en)$_2$(dma)$_2$] (ClO$_4$)$_3$	F	8.0	22.0	5.3	12.8	16.6		
	C	8.0	22.4	5.3	13.0	16.5		
cis-[Cr(en)$_2$(dmso)$_2$] (ClO$_4$)$_3$	F	8.3	15.4	4.4	8.9	16.8		10.1
	C	8.3	15.3	4.5	8.9	17.0		10.2
cis-[Cr(en)$_2$(dmf)$_2$] (ClO$_4$)$_3$	F	8.4	19.1	4.9	13.4	17.3		
	C	8.4	19.5	4.9	13.6	17.3		
cis-[Cr(en)$_2$(dmf)$_2$] (ClO$_4$)$_2$NO$_3$·H$_2$O	F	8.7			15.9	11.9		
	C	8.7			16.4	11.9		
cis-[Cr(en)$_2$(dmso)(dma)] (ClO$_4$)$_2$NO$_3$	F	8.8	20.1	5.2	14.1	11.8		5.2
	C	8.7	20.1	5.2	14.1	11.9		5.4
cis-[Cr(en)$_2$(dmf)(dmso)] (ClO$_4$)$_2$NO$_3$·H$_2$O	F		17.4	4.6	11.2	17.1		5.2
	C		17.3	4.7	11.3	17.1		5.1
cis-[Cr(en)$_2$(dmf)(dmso)] (ClO$_4$)$_2$NO$_3$·H$_2$O	F		18.5	4.6	13.9	12.0		5.4
	C		18.0	5.2	14.0	11.8		5.3
trans-[Cr(en)$_2$(dmso)(ONO)] (ClO$_4$)$_2$	F	10.6	14.5	4.5	13.9	14.4		6.3
	C	10.5	14.6	4.5	14.1	14.3		6.5

TABLE I. *(continued)*

Complex		Cr	C	H	N	Cl	Br	S
cis-[Cr(NH$_3$)$_4$(OH$_2$)Cl] (ClO$_4$)$_2$	F			3.8	14.6	29.0		
trans-[Cr(NH$_3$)$_4$(OH$_2$)Cl] (ClO$_4$)$_2$	F	14.0		3.8	14.7	29.0		
	C	14.0		3.8	15.0	28.6		
cis-[Cr(NH$_3$)$_4$(OH$_2$)Cl] Br$_2$	F	15.8		4.2	17.2	10.6	47.9	
	C	15.6		4.2	16.8	10.9	47.9	
cis-[Cr(NH$_3$)$_4$(dmso)Cl] (ClO$_4$)$_2$	F	11.9	5.6	4.3	12.6	24.5		7.9
trans-[Cr(NH$_3$)$_4$(dmso)Cl] (ClO$_4$)$_2$	F		5.7	4.2	12.6	24.4		7.5
	C	12.0	5.6	4.2	13.0	24.6		7.8
cis-[Cr(NH$_3$)$_4$(dma)Cl] (ClO$_4$)$_2$	F	12.1	10.6	4.6	15.8	23.9		
	C	11.8	10.9	4.8	15.9	24.1		
cis-[Cr(NH$_3$)$_4$(dmf)Cl] (ClO$_4$)$_2$	F	12.1	8.4	4.4	16.5	24.5		
	C	12.2	8.4	4.5	16.4	24.9		
cis-[Cr(NH$_3$)$_4$(dmso)$_2$] (ClO$_4$)$_3$	F		8.6	4.2	9.60	18.9		11.1
	C		8.4	4.2	9.75	18.5		11.2
[Hg(dmso)$_6$] (ClO$_4$)$_2$	F	23.6[b]	17.0	4.1		8.1		22.2
	C	23.2[b]	16.6	4.2		8.2		22.2

[a] F = found, C = calculated (%). [b] Hg figures.

TABLE II. Selected I.R. Band Frequencies (cm^{-1}) of Some Solvent Containing Chromium(III) Complexes.

Complex[a]	$\nu_{S=O}$	$\nu_{C=O}$	$\nu_{O=C=N}$
cis-Cr(en)$_2$(dma)Cl^{2+}	–	1615	760
cis-Cr(en)$_2$(dmf)Cl^{2+}	–	1655	735
cis-Cr(en)$_2$(dmso)Cl^{2+}	965	–	–
trans-Cr(en)$_2$(dmso)Cl^{2+}	971	–	–
cis-Cr(en)$_2$(dma)$_2^{3+}$	–	1610	760
cis-Cr(en)$_2$(dma)(dmso)$^{3+}$	960	1620	745
trans-Cr(en)$_2$(dmso)Br^{2+}	990	–	–
trans-Cr(en)$_2$(dmso)ONO^{2+}	962	–	–
trans-Cr(en)$_2$(dmso)(OH$_2$)$^{3+}$	980	–	–
cis-Cr(en)$_2$(dmso)$_2^{3+}$	988	–	–
cis-Cr(NH$_3$)$_4$(dma)Cl^{2+}	–	1612	763
cis-Cr(NH$_3$)$_4$(dmf)Cl^{2+}	–	1666	785
cis-Cr(NH$_3$)$_4$(dmso)Cl^{2+}	945	–	–
trans-Cr(NH$_3$)$_4$(dmso)Cl^{2+}	960	–	–
cis-Cr(NH$_3$)$_4$(dmso)$_2^{3+}$	960	–	–
DMSO	1055[b]	–	–
DMA	–	1695[c]	730[c]
DMF	–	1714[c]	660[c]

[a]Usually halide salts, to avoid complications from overlapping ClO$_4^-$ bands. [b]Value for liquid phase (W.D. Horrocks and F. A. Cotton, *Spectrochim. Acta*, *17*, 134 (1961)). [c]Value for gas phase (C. V. Berney and J. H. Weber, *Inorg. Chem.*, *7*, 283 (1968)).

was gassed with dry NH$_3$ gas for ~5 min. Aliquots diluted with water were titrated (methyl orange) against standardized HNO$_3$ (*ca.* 0.0100 *M*). Other aliquots were then diluted (DMSO) exactly until in the range (0–2) × 10^{-4} *M* in NH$_3$. The absorbance of 2 ml of these samples containing PBF (*ca.* 4 mg) was recorded. The resultant graph of absorbance *vs.* [NH$_3$] was linear, indicating adherence to the Beer–Lambert law at least in this [NH$_3$] range (ϵ_{353}^{max} = 1.90 × 10^4 *M*$^{-1}$ cm^{-1} for the basic form of PBF). This method for DMSO is an adaption of that designed to detect basic impurities in DMF [25]. The acid form of PBF (prepared as directed [26]) is transparent at 353 nm but its basic form is intensely absorbing; an excess of PBF is used to convert moderately strong base (*e.g.*, NH$_3$) quantitatively into a light absorbing equivalent.

TABLE III. Data for Chloride Release from Some cis-CrN$_4$(sol)Cl^{2+} Complexes in DMSO at 40 °C.

cis Complex	$t_{1/2}$, min[a]	% Free Cl$^-$ at times:[b]				
($10^2 C_o$, M)		{20,	40,	60,	80	100 min }
Cr(en)$_2$(dmf)Cl^{2+} (2.4–2.8)	25	0.4	1.2	2.0	2.6	
Cr(en)$_2$(dma)Cl^{2+} (1.2–1.3)	20	2.0	3.1	3.9	4.3	4.2
Cr(en)$_2$(dmso)Cl^{2+} (1.1–1.8)		2.4[c]	4.4[c]	4.5[c]	4.8[c]	
		{70,	140,	210,	280,	350 min }
Cr(NH$_3$)$_4$(dmf)Cl^{2+} (4.3–3.8)	200	0.1$_5$	0.3	0.6	0.7	
Cr(NH$_3$)$_4$(dma)Cl^{2+} (2.5–2.7)	70	0.8$_5$	1.2	1.4	1.6	
Cr(NH$_3$)$_4$(OH$_2$)Cl^{2+} (6.0–6.7)	70	6.0[c] (0.1)[d]	7.6[c] (0.3)[d]	8.4[c] (0.6)[d]	9.1[c] (0.8)[d]	8.9[c] (0.8)[d]
Cr(NH$_3$)$_4$(dmso)Cl^{2+}		0.4	0.4$_5$	0.6	0.8	0.8

[a]Estimated half-life of solvent interchange of the starting complexes at 40 °C.   [b]Corrected for Cl$^-$ release during the ion exchange separations.   [c]Mean of duplicate determinations.   [d]Solvent: DMSO, 1% v/v in 0.3 M HClO$_4$.

TABLE IV. Observed and Predicted Isosbestic Points for Solvent Interchange of Some cis-CrN$_4$(sol)Cl^{2+} Complexes in DMSO.

Complex	λ, nm (ϵ, M^{-1} cm^{-1})		% Steric Change
	Observed	Predicted	
cis-Cr(NH$_3$)$_4$(OH$_2$)Cl^{2+}	397 (36.0) 444 (10.4) 500 (36.8)	398 (35.6) 445 (10.1) 500 (37.0)	<2%
cis-Cr(NH$_3$)$_4$(dmf)Cl^{2+}	399 (34.4) 444 (10.4) 545 (43 ± 5)	399 (34.8) 442 (10.6) 546 (42.5 ± 0.5)[a]	<4%
cis-Cr(NH$_3$)$_4$(dma)Cl^{2+}	~360 (~15)	365 ± 5 (18 ± 3)[a]	<4%
cis-Cr(en)$_2$(OH$_2$)Cl^{2+}	393 (69.1)[b] 445 (23.5) 496 (72)[b]	392 (68.9) 443 (23.0) 495 (73 ± 2)[a]	<2%
cis-Cr(en)$_2$(dmf)Cl^{2+}	392 (68.3)[b] 441 (23.4) 525 (84.9)	391 (68.0) 441 (23.2) 523 (85.5)	<2%
cis-Cr(en)$_2$(dma)Cl^{2+}	376 (52.0)[b]	375 ± 1 (50 ± 2)[a]	<2%

[a]Ill-defined; near tangential intersection of spectra.   [b]Initial position; shows small drift of $ca.$ 0.5–1 nm to longer wavelengths during reaction.

Results and Preliminary Discussion

1. Solvolysis of Solvento Complexes

Cis-$Cr(NH_3)_4(sol)Cl^{2+}$ ($sol = OH_2$, $dmso$) in $DMSO$

The changes in visible spectra accompanying the sol = OH$_2$ reaction are complex. For DMSO solutions 1% v/v in HClO$_4$ (0.3 M) however ($vide$ $infra$), these changes simplify into two stages (Fig. 1). Insignificant Cl$^-$ loss was established for the first step by direct determination (Table III). Locations of the isosbestic points (Fig. 1, Table IV) readily identify this first step as:

cis-Cr(NH$_3$)$_4$(OH$_2$)Cl^{2+} + DMSO → cis-Cr(NH$_3$)$_4$-(dmso)Cl^{2+} + H$_2$O. All three points are definitive of stereochemical course and allow at most 4% $trans$-
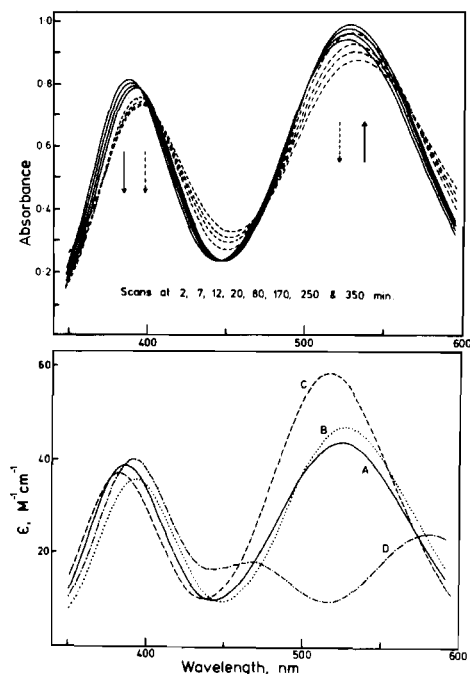
Figure 1. Upper: Spectral changes accompanying reaction of *cis*-Cr(NH₃)₄(OH₂)Cl²⁺ in DMSO (1% in 0.3 *M* HClO₄) at 55 °C. Lower: Pure component spectra in DMSO: A, *cis*-Cr(NH₃)₄(OH₂)Cl²⁺; B, *cis*-Cr(NH₃)₄(dmso)Cl²⁺; C, *cis*-Cr(NH₃)₄(dmso)₂³⁺; D, *trans*-Cr(NH₃)₄(dmso)Cl²⁺.

Figure 2. Spectral changes characterizing reaction of *cis*-Cr(NH₃)₄(dmso)Cl²⁺ in DMSO at 60.2 °C.

Cr(NH₃)₄(dmso)Cl²⁺. The second and much slower step arises from reaction of the first formed product; essentially identical spectral changes are observed for an authentic *cis*-Cr(NH₃)₄(dmso)Cl²⁺ sample reacting under comparable conditions (Fig. 2). Indeed, at six $t_{1/2}$ *cis*-Cr(NH₃)₄(OH₂)Cl²⁺ reaction, the spectrum closely corresponds to *cis*-Cr(NH₃)₄(dmso)Cl²⁺, confirming the isosbestic point results. Any coformed (>4%)* *trans* product would be readily detected since its spectrum (Fig. 1) differs widely. Moreover, as the separate investigations reveal (*vide infra*), this or the *trans*-aquochloro species are not formed even transiently.

The second step itself is complex (Fig. 2). Isosbestic points at ~360, 410, 482 and 570 nm are indistinct and persist for short reaction times only. These spectral changes are incompatible with halide release and/or isomerization (Fig. 1). Direct Cl⁻ loss determination (Table III) confirms the former conclusion. NH₃ loss was detected with PBF. Plots of ln-[NH₃] *vs.* time gave $k_N = 4 \times 10^{-5}$ sec⁻¹ for first order release over 4 hr at 65 °C (duplicate runs). Note that this rate corresponds to only ~2% NH₃ release from the product over four $t_{1/2}$ of *cis*-Cr(NH₃)₄-(OH₂)Cl²⁺ solvent interchange in DMSO (1% v/v

in 0.3 *M* HClO₄), assuming $\Delta H^{\ddagger} = 25$ kcal mol⁻¹ for k_N. No attempt was made to characterize triammine complexes and investigate further but it can be seen that initial spectral changes (Fig. 2) are at least qualitatively those expected for NH₃ loss; a general loss in intensity [8] and shifts in maxima to lower energies [8] are observed.

Cis-Cr(NH₃)₄(OH₂)Cl²⁺ in unacidified DMSO undergoes significant parallel reaction. Cl⁻ loss is fast and extensive (Table III). 6% NH₃ loss (PBF) also occurs during the first four $t_{1/2}$ of the concurrent solvent interchange reaction (*cf.* <2% in acidified DMSO*). *Cis*-Cr(NH₃)₄(OH)Cl⁺ participation is indicated; reactant deprotonation is not unexpected in basic DMSO [27] although this does not occur to any observable extent (other than in reactivity) since the spectrum of *cis*-Cr(NH₃)₄(OH₂)Cl²⁺ in DMSO with or without HClO₄ (1% v/v, 0.3 *M*) is the same (±0.5%). This suggestion is supported by the observation that Cl⁻ and NH₃ release paths are suppressed in acid medium, and by the well-known fact that hydroxo complexes are several orders of magnitude more reactive than their aquo counterparts. Also meriting mention are the highest extent of Cl⁻ release (~9%, Table III) which is about ten times the DMSO equilibrium figure (0.8%), and the absence of a sharp fall in this figure for solutions aged for lengthy periods. These results imply that Cl⁻ release *via* *cis*-Cr(NH₃)₄(OH)Cl⁺ solvolysis is largely irreversible and that this comes to an abrupt halt as the precursor aquo complex is consumed through solvent interchange. The appreciable NH₃ loss deterred efforts to directly generate *cis*-Cr(NH₃)₄-(OH)Cl⁺ (aqua complex + N(C₂H₅)₄OH in DMSO) and investigate further.

First order rate constantas for solvent interchange (k_s, ±5%) are given in Table V. Plots of ln |D − D∞| *vs.* time were linear over 60% reaction (360 nm) for

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*Kinetic overlap from the second stage of reaction precluded better definition. No positive evidence for *trans* product was obtained.

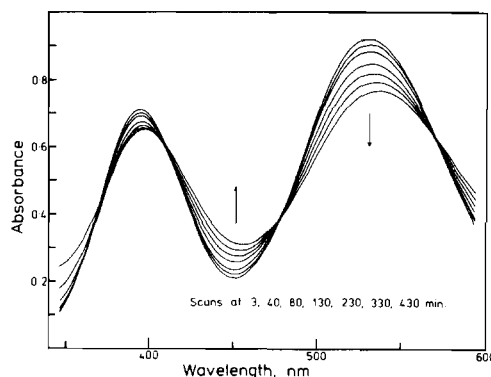*Estimated. The PBF amine detection method is not applicable to acid media.

TABLE V Rate Data for the Reaction cis-$Cr(NH_3)_4$ (sol)-Cl^{2+} + DMSO → cis-$Cr(NH_3)_4(dmso)Cl^{2+}$ + SOL

(i) sol = OH_2, C_o = (5 8–7 0) × 10^{-2} M^a

$10^4 k_s$, sec^{-1}	T, °C	$10^4 k_s$, sec^{-1}	T, °C
0 47[b]	29 7	2 12	41 0
0 44[b]	"	5 46	49 7
0 41[b]	"	5 25	49 8
0 42[b]	29 8	5 24	49 9
0 47[b,c]	"	5 85	50 0
0 44[b,d]	"	5 64	50 1
1 54	39 5	5 50	50 3
1 68	39 7	5 91	50 8

(ii) sol = dmf, C_o = (4 2–4 7) × 10^{-2} M

$10^4 k_s$, sec^{-1}	T, °C	$10^4 k_s$, sec^{-1}	T, °C
0 39[a]	36 0	1 13	46 5
0 35[a]	"	3 08	55 6
0 48[a]	36 4	3 26	56 2
0 38[a]	"	4 11	56 3
0 37[a]	"	3,69	57 0
0 41[a]	"	3 64	57 0
0 41[a]	"	3 77	57 5
0 96	44 6	4 04	57 9
0 96	45 0	4 05	58 1
1 03	46 5		

(iii) sol = dma, C_o = (2 3–2 5) × 10^{-2} M

$10^4 k_s$, sec^{-1}	T, °C	$10^4 k_s$, sec^{-1}	T, °C
0 55[a]	29 7	1 66	39 8
0 43[a]	"	1 53	"
0 46[a]	"	5 00	50 0
0 49[a]	30 0	5 28	"
0 48[a]	"	5 40	"
0 46[a]	"	5 59	50 1
1 79	39 5	5 37	"
1 43	39 6	5 21	50 2
1 51	39 7	5 22	50 4

[a]Solvent 1% v/v in 0 3 M aq $HClO_4$ [b]Sampling method (see Experimental) [c]Solvent, 1% v/v in 0 15 M aq $HClO_4$ [d]C_o = 6 5 × 10^{-2} M, μ= 0 40 ($NaClO_4$)
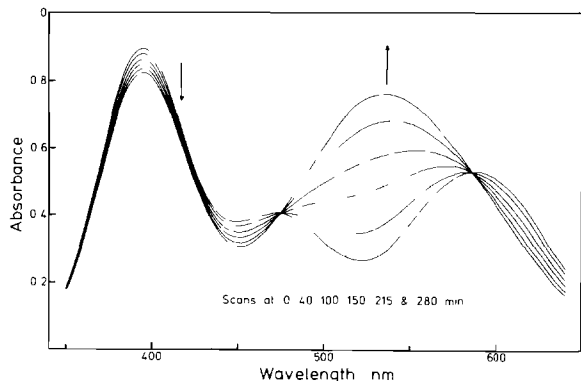
Figure 3 Spectral changes characterizing reaction of $trans$-$Cr(NH_3)_4(dmso)Cl^{2+}$ in DMSO at 59 8 °C

acidified DMSO runs ϵ changes for the first step are not large ($\sim$7 M^{-1} cm^{-1}, Fig 1), thus the wavelength chosen necessarily corresponded to relatively small absorbance changes for the (slower) secondary reaction k_s values are constant over 0 01–0 03 M $HClO_4$ and over a twofold change in ionic strength The numbers (Table V) apply strictly to 1% aqueous DMSO but undoubtedly [28] differ negligibly to those for neat DMSO (vide infra)

$Trans$-$Cr(NH_3)_4(dmso)Cl^{2+}$ and -$Cr(NH_3)_4(OH_2)$-Cl^{2+} in DMSO

The first stage of the composite spectral changes accompanying $trans$-$Cr(NH_3)_4(dmso)Cl^{2+}$ reaction in DMSO is shown in Fig 3 Simple isomerization is the dominant path, isosbestic points at 477 and 584 nm tolerably match those expected (475 and 579 nm, Fig 1) Some direct NH_3 loss is apparent in the small but significant discrepancies [8], a fact confirmed by tests with PBF Both points drift at longer reaction times and the form of the cis-$Cr(NH_3)_4(dmso)Cl^{2+}$ spectrum is not attained Rate plots (530 nm) for the first stage yield k_{tc} = (5 8 ± 0 6) × 10^{-5} sec^{-1} at 59 8 °C (duplicate runs) which is only one-fifth the rate of NH_3 loss from the cis-$Cr(NH_3)_4(dmso)Cl^{2+}$ product, hence the early kinetic overlap in the two steps Preliminary runs on $trans$-$Cr(NH_3)_4(OH_2)Cl^{2+}$ in DMSO (1% v/v in 0 3 M $HClO_4$) revealed a similar complexity, again with slow isomerization the dominant path These results clearly rule out two less likely alternate pathways for cis solvent interchange (vide supra)

$$cis\text{-}Cr(NH_3)_4(OH_2)Cl^{2+} \xrightarrow{\text{slow}} trans\text{-}Cr(NH_3)_4\text{-}$$
$$(OH_2)Cl^{2+} \xrightarrow[\text{DMSO}]{\text{fast}} cis\text{-}Cr(NH_3)_4(dmso)Cl^{2+}$$

$$cis\text{-}Cr(NH_3)_4(OH_2)Cl^{2+} \xrightarrow[\text{DMSO}]{\text{slow}} trans\text{-}Cr(NH_3)_4\text{-}$$
$$(dmso)Cl^{2+} \xrightarrow{\text{fast}} cis\text{-}Cr(NH_3)_4(dmso)Cl^{2+}$$
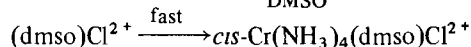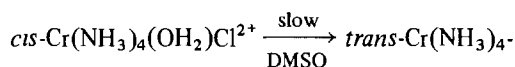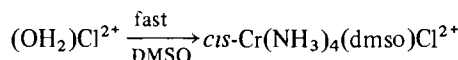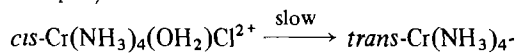
Moreover the accumulation of the unobserved $trans$ complexes can be precluded on kinetic grounds since they are consumed at only a fraction $\sim$1/100, 60 °C) of the cis solvent interchange rate

Cis-$Cr(NH_3)_4(sol)Cl^{2+}$ (sol = dmf, dma) in DMSO

Again two steps characterize these reactions, the first being retentive solvent interchange (Table IV) and the second NH_3 loss from the common cis-$Cr(NH_3)_4(dmso)Cl^{2+}$ product Neat DMSO was employed as experiment showed no effect of added $HClO_4$ on either spectra or kinetics, facts attributable to the absence of appreciable acidic or basic properties of the O-bound aprotic solvents (cf OH_2) *

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*N-bound amides do show significant acid/base properties

TABLE VI. Rate Data for the Reaction: *cis*-Cr(en)$_2$(sol)Cl^{2+} + DMSO → *cis*-Cr(en)$_2$(dmso)Cl^{2+} + SOL.

(i) sol = OH$_2$; C$_o$ = (2.3–3.3) × 10^{-2} M[a]

10^3 k$_s$, sec^{-1}	T, °C	10^3, k$_s$, sec^{-1}	T, °C
0.31	30.4	2.65	47.7
0.35	30.5	2.76	48.4
0.34	30.5	3.09	48.6
0.59	35.4	2.76	48.6
0.60	35.4	3.25	49.1
0.73	36.1	4.36	52.2
0.73	36.2	4.50	52.2
2.03	44.9	4.79	52.3
2.04	44.9		

(ii) sol = dmf; C$_o$ = (1.8–2.6) × 10^{-2} M

10^3 k$_s$, sec^{-1}	T, °C	10^3, k$_s$, sec^{-1}	T, °C
0.17	34.2	1.06	49.6
0.25	36.6	2.12	55.7
0.24	36.7	2.07	55.8
0.54	43.3	2.87	58.7
0.53	43.6	2.75	58.9
1.03	49.4	2.78	58.9
1.09	49.6		
1.08[a]	49.6		

(iii) sol = dma; C$_o$ = (1.0–1.5) × 10^{-2} M

10^3 k$_s$, sec^{-1}	T, °C	10^3 k$_s$, sec^{-1}	T, °C
0.24	32.1	1.35	46.9
0.23	32.1	1.34	46.9
0.40	34.7	2.88	53.4
0.37	35.3	2.89	53.4
0.39	35.3	2.93	54.7
0.45	37.2	3.34	54.8
0.45	37.3	3.35	55.2
0.77	41.9	3.63	57.0
0.83	41.9	3.81	57.2
0.81[a]	41.9		
0.83[a]	41.9		

[a]Reactant supplied as bromide salt.

Greater kinetic overlap between the two steps here arises from the slower interchange rates. This problem was reduced by collecting data at 482 nm, an initial "isosbestic point" for secondary reaction. With sol = dma, interference arose from the need to take measurements in the region of the absorption maximum (530 nm). Rate constants were calculated in this case from the initially linear portion (one t$_{1/2}$) of rate plots curving appreciably after *ca.* two t$_{1/2}$. The results are included in Table V.

Cis-Cr(en)$_2$(sol)Cl^{2+} (sol = OH$_2$, dmf, dma, dmso) in DMSO

Cl$^-$ loss from the parent ions is not significant; a maximum of free Cl$^-$ (5%) is reached only at equilibrium [30] (Table III) (*cf. cis*-Cr(NH$_3$)$_4$(OH$_2$)Cl^{2+}). The data indicates that this follows the faster solvent interchange reactions which give initially *cis*-Cr(en)$_2$-(dmso)Cl^{2+} and, after nine t$_{1/2}$, 95% *cis*-Cr(en)$_2$-(dmso)Cl^{2+} and 5% *cis*-Cr(en)$_2$(dmso)$_2^{3+}$ in each case. All reactions are highly retentive (Table IV); *trans* intermediates are again ruled out — k$_{tc}$ for *trans*-Cr-(en)$_2$(dmso)Cl^{2+} is ~10^{-4} sec^{-1} at 60 °C [9], an isomerization too slow to prevent its detection if formed (>2%). *Trans*-Cr(en)$_2$(OH$_2$)Cl^{2+} isomerizes at least as slowly and the unlikely possibility of pre-isomerization is therefore eliminated.

In contrast to *cis*-Cr(NH$_3$)$_4$(OH$_2$)Cl^{2+}, no significant Cl$^-$ loss was apparent for runs on *cis*-Cr(en)$_2$-(OH$_2$)Cl^{2+} in the absence of HClO$_4$ (neat DMSO, spectrophotometric and potentiometric results). This is difficult to attribute to a higher pK$_a$ for the aquobis(ethylenediamine) complex in DMSO. The results require an increase of ~0.5–1.0 pK$_a$ units, the reverse of trends established for similar complexes in aqueous media [29]. More likely the Cl$^-$ loss parallel path is less significant *both* because of the increased solvent interchange rate and reduced rate of Cl$^-$ solvolysis. Unpublished observations on Cr(NH$_3$)$_4$ and Cr(en)$_2$ analogues reveal that, for neutral leaving groups, the en complexes are more reactive (by a factor of approximately ten) while for anionic leaving groups the reverse is true, in accord with this rationale. We note also that amine loss from the *cis*-chloro(dmso) product appears to be less significant in the chelating (en) system. This is at least partly due to the difference in time scales for the (NH$_3$)$_4$ and (en)$_2$ experiments, rather than a real difference in rates of Cr–N cleavage; the (en)$_2$ complexes interchange solvent more rapidly. Moreover, the *cis*-(en)$_2$ species are thermodynamically stable in these solvents [8, 30]. Note that in aqueous systems NH$_3$ release is usually slower than hydrolysis of en (*vide infra*, Table XVIII).

Fixed wavelength scans were performed at 368 (sol = OH$_2$), 472 (dmf) and 520 nm (dma). Rate constants were calculated according to the Guggenheim procedure [31] for data covering the first and fourth half-lives (t$_{1/2}$ > 10 min). For faster reactions conventional plots were made, ln | D − D$_\infty$ | *vs.* time, where D$_\infty$ was observed or calculated. Equivalent results (Table VI) were obtained from these plots which were of good linearity over two t$_{1/2}$, provided corrections were applied for subsequent *cis*-Cr(en)$_2$(dmso)Cl^{2+} Cl$^-$ release, where this was appropriate.

Cis-Cr(en)$_2$(OH$_2$)Cl^{2+} was by necessity provided as the bromide salt. However added LiBr (2 equiv) had no effect on the other two reactions (sol = dmf,

TABLE VII. Rate Data for the Reaction; cis-Cr(en)$_2$(dmso)-(dma)$^{3+}$ + DMSO $\xrightarrow{k_{s_2}}$ cis-Cr(en)$_2$(dmso)$_2^{3+}$ + DMA.

$10^3\ k_{s_2}$, sec^{-1}	T, °C	$10^3\ k_{s_2}$, sec^{-1}	T, °C
0.24	20.0	0.74	30.3
0.23	20.1	1.29	35.2
0.24	20.3	1.29	35.3
0.42	24.9	1.16	"
0.42	25.3	1.78	37.9
0.42	"	1.68	38.1
0.58	28.2	1.68	"
0.69	30.1	1.97	39.8
0.75	30.3	2.07	"
0.75	"	2.14	40.0

C_o = (1.01–1.27) $\times$ 10^{-2} M; k_{s_2} values are from runs at 506 nm. Reactant supplied as solid salt.

dma) and therefore k_s values here are not expected to differ to those appropriate to the perchlorate salt.

Cis-Cr(en)$_2$(dma)$_2^{3+}$ and -Cr(en)$_2$(dma)(dmso)$^{3+}$ in DMSO

The reaction of the *bis*(dma) species necessarily occurs stepwise:

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

$$+\ \text{DMA} \xrightarrow{\text{DMSO}} cis\text{-Cr(en)}_2\text{(dmso)}_2^{3+} + 2\text{DMA}$$
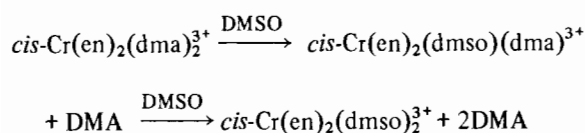
A typical run commencing with cis-Cr(en)$_2$(dma)$_2^{3+}$ (Fig. 4) reveals no isosbestic points; this arises because dmso substitution of dma leads to significantly decreased ϵ^s without change in ligand field. An overall absorbance decay is observed in accordance with the three *cis* species (Fig. 4). Similar changes are displayed by solutions of cis-Cr(en)$_2$(dmso)-(dma)$^{3+}$, isolated to separately investigate the second step. The final spectrum from both reactants corresponds closely to cis-Cr(en)$_2$(dmso)$_2^{3+}$, assuring that both steps are retentive. At 506 nm, ϵ *cis* = 100 and ϵ *trans* = 12 M^{-1} cm^{-1} for Cr(en)$_2$(dmso)$_2^{3+}$. Slight variations in D_∞ values from run to run would therefore permit at most 4% *trans* product. Again, the intermediacy of *trans* species may be ruled out on the basis of reactivity and the fact that en loss (~20%) accompanies their slow isomerization [9]; no en loss occurs in the time scale of the present experiments.

The equilibrium composition 95% cis-Cr(en)$_2$-(dmso)$_2^{3+}$, 5% Cr(en)(dmso)$_4^{3+}$ (and 5% en) has been measured [4].

Rate constants from conventional first order plots (506 nm) for cis-[Cr(en)$_2$(dmso)(dma)] (ClO$_4$)$_2$NO$_3$ reactant are given in Table VII. In the case of cis-[Cr(en)$_2$(dma)$_2$](ClO$_4$)$_3$, the two step nature of the

TABLE VIII. Rate Data[a] for the Reaction: cis-Cr(en)$_2$-(dma)$_2^{3+}$ $\xrightarrow[\text{DMSO}]{k_{s_1}}$ cis-Cr(en)(dmso)(dma)$^{3+}$ + DMA $\xrightarrow[\text{DMSO}]{k_{s_2}}$ cis-Cr(en)$_2$(dmso)$_2^{3+}$ + 2DMA.

$10^3\ k_{s1}$, sec^{-1}	$10^3\ k_{s2}$, sec^{-1}	T, °C
0.86	0.24	21.8
0.77	0.26	"
0.88	0.26	"
0.80	0.25	"
0.84	0.26	"
2.4	0.52	28.7
1.8	0.58	28.8
2.2	0.59	29.3
3.1	0.75	32.6
2.8	0.78	32.7
–	1.14[b]	35.3
–	1.37[b,c]	"
4.4	1.24	36.3
4.5	1.13	36.5
6.5[d]	1.78	39.3
6.6[d]	1.84	39.5
6.2[d]	1.84	"
5.4[d]	1.75	"
7.0[d]	1.80	"

[a]C_o = (0.89–1.01) $\times$ 10^{-2} M.   [b]C_o = 9.4 $\times$ 10^{-3} M.   [c]9.4 $\times$ 10^{-3} M in NaNO$_3$.   [d]Uncertainty: ±20% (see text).
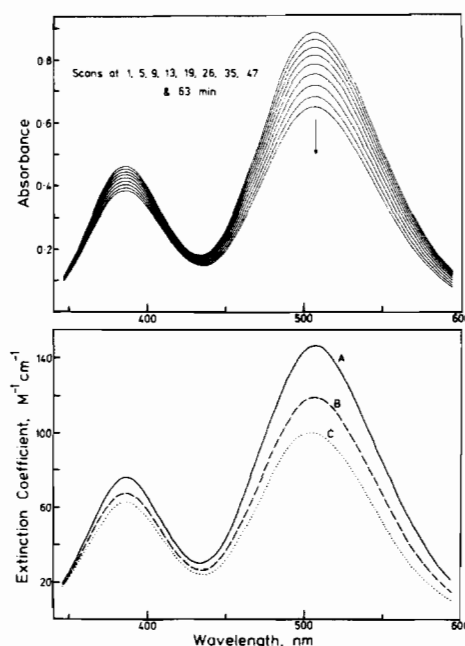

Figure 4. Upper: Spectral changes characterizing solvent interchange of cis-Cr(en)$_2$(dma)$_2^{3+}$ in DMSO at 28.7 °C. Lower: Pure component spectra in DMSO: A, cis-Cr(en)$_2$-(dma)$_2^{3+}$; B, cis-Cr(en)$_2$(dmso)(dma)$^{3+}$; C, cis-Cr(en)$_2$-(dmso)$_2^{3+}$.

TABLE IX. Observed and Predicted Isosbestic Points for the Reactions: cis-Cr(en)$_2$(dmf)$_2^{3+}$ $\xrightarrow{\text{DMSO}}$ cis-Cr(en)$_2$(dmf)-(dmso)$^{3+}$ + DMF. $\lambda(\epsilon)$, nm(M^{-1} cm^{-1})

Observed	Predicted[a]
513 (100.4)	512 (100.0)
424 (25.6)	423 (25.4)
380 (66.1)	380 (65.8)

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

519 (92.6)	520 (91.8)
428 (26.0)	426 (25.7)
388 (61.5)	388 (61.0)

[a]For 100% retention.   [b]Reactant solid complex; similar data obtained for two other methods for studying reaction.
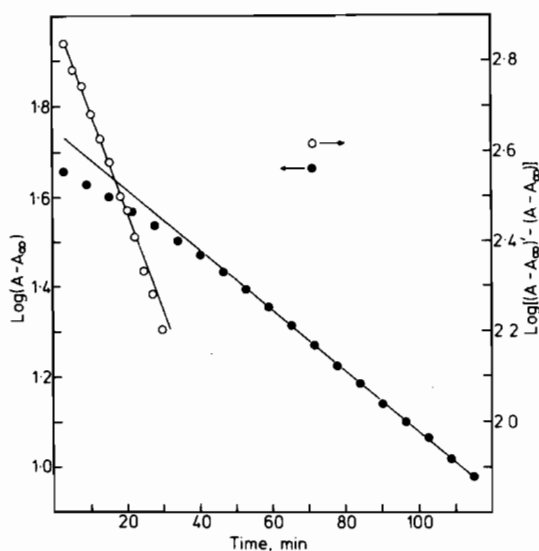
Figure 5. Sample rate plot for the solvent interchange of cis-Cr(en)$_2$(dma)$_2^{3+}$ in DMSO. C_o = 9.6 × 10^{-3} M; T = 21.8 °C; constant λ = 506 nm.

TABLE X. First Order Rate Constants for the Reactions: cis-Cr(en)$_2$(dmf)$_2^{3+}$ $\xrightarrow[\text{DMSO}]{k_{s1}}$ cis-Cr(en)$_2$(dmso)(dmf)$^{3+}$ + DMF

T, °C	10^3 k_{s1}, sec^{-1}[a]
51.0	11.3
50.4	10.4
45.3	8.5
45.2	7.8
40.6	6.0
40.4	6.0

cis-Cr(en)$_2$(dmso)(dmf)$^{3+}$ $\xrightarrow[\text{DMSO}]{k_{s2}}$ cis-Cr(en)$_2$(dmso)$_2^{3+}$ + DMF

T, °C	10^4 k_{s2}, sec^{-1}[b]	T, °C	10^4 k_{s2}, sec^{-1}[c]
51.0	40.7	51.6	47.7
50.4	36.3	51.5	50.2
45.3	26.2	47.0	33.7
45.2	26.5	47.0	32.0
43.0	18.8	40.0	16.6
40.6	15.6	39.9	17.0
40.4	15.5	34.6	9.2
36.1	9.6	30.4	6.30
35.9	9.1	30.4	6.28
31.7	5.02	25.7	3.70
31.7	5.03	26.0	3.77[d]
26.0	3.35[e]	26.0	3.65
25.9	3.18	25.2	3.38
26.0	3.50[f]	20.3	2.03

[a]k_{s1} values (±20%) below 40.4 °C not recorded; graphical calculation (see text) becomes inaccurate in the range 20–40 °C.   [b]Calculated for secondary reaction commencing with cis-[Cr(en)$_2$(dmf)$_2$](ClO$_4$)$_3$.   [c]Calculated for secondary reaction following Hg^{2+} ([Hg(dmso)$_6$](ClO$_4$)$_2$) promoted solvolysis of Br$^-$ from cis-[Cr(en)$_2$(dmf)Br]-(ClO$_4$)$_2$ in DMSO. [complex]$_0$ = (7–10) × 10^{-3} M, [Hg^{2+}]$_0$ = 0.05 M.   [d][Hg^{2+}]$_0$ = 0.10 M.   [e]cis-[Cr(en)$_2$(dmso)-(dmf)](ClO$_4$)$_3$ reactant.   [f]cis-[Cr(en)$_2$(dmso)(dmf)](ClO$_4$)$_2$·NO$_3$·H$_2$O reactant.

reaction is clearly evident in early curvature of plots of ln | D − D$_\infty$ | $vs.$ time, where D$_\infty$ corresponds to cis-Cr(en)$_2$(dmso)$_2^{3+}$ (Fig. 5). Both k_{s_1} and k_{s_2} were obtained under all conditions by a conventional treatment [32] and the results are recorded in Table VIII. Note that evaluation of the faster rate constant (in this case − but not necessarily [32] − k_{s_1}) is contingent upon early curvature of the rate plot [32]. Because this curvature is not marked (Fig. 5) and also because it is sensitive to early time reaction disturbances (*e.g.*, incomplete thermal equilibration, instrument damping), the precision of k_{s_1} is low (±10% generally, ±20% at uppermost temperatures).

Assignment of fast and slow steps provided an ambiguity [32] which was resolved by direct measurement of k_{s_2} commencing with cis-Cr(en)$_2$-

(dmso)(dma)$^{3+}$ (*vide supra*). The correct assignment (fast−slow) is also established by matching ϵ_{obs} with ϵ_{calc} for the mixed solvento complex [32]. Note the minor but systematic differences between the two sets of k_{s_2} values (Table VII and VIII); those obtained directly are greater by approximately 20%. However, k_{s_2} values obtained indirectly are increased by 20% in the presence of NaNO$_3$ (one equiv), and therefore a specific nitrate medium effect is indicated. This we attribute to significant nitrate ion pairing (added NaClO$_4$ has a negligible effect). No evidence for nitrate coordination was obtained.

Cis-Cr(en)$_2$(dmf)$_2^{3+}$ and -Cr(en)$_2$(dmso)(dmf)$^{3+}$ in DMSO

These reactions closely parallel those described immediately above and similar considerations apply.

TABLE XI Rate Data for the Solvent Interchange of _cis_-Cr-(en)$_2$(dmso$_2^{3+}$ in DMF

T, °C	$10^4\ k_{s1}$, sec^{-1}	$10^4\ k_{s2}$, sec^{-1}
50 3	~75[a]	37 3
50 0	~70[a]	35 7
45 8	~52[a]	26 2
40 0	38 0	12 4
36 3	37 0	9 8
36 2	33 0	9 4

[a]Estimated from k_{s2} and the relation $(\epsilon_A - \epsilon_C)/(\epsilon_B - \epsilon_C) = k_{s_1}/(k_{s_2} - k_{s_1})$ (see text), ±50%, others ±20%

TABLE XII Isosbestic Points for Solvent Interchange of _cis_-Cr(en)$_2$(dma)$_2^{3+}$ in Perchloric Acid

Observed λ, nm (ϵ, $M^{-1}\ cm^{-1}$)	Predicted[a] λ, nm (ϵ, $M^{-1}\ cm^{-1}$)
366 (49 4)[b]	365 (48 4)
441 (~29)[b]	—
452 (~41)[b]	—
354 (34 4)[c]	354 (34 6)
433 (21 1)[c]	432 (21 5)
454 (42 0)[c]	454 (42 3)

[a]Predicted positions assume 100% stereoretention [b]At t = 0 (extrapolated) with _cis_-Cr(en)$_2$(dma)$_2^{3+}$ as precursor [c]Values for second step, Cr(en)$_2$(dma)(OH$_2$)$^{3+}$ generated by _cis_-Cr(en)$_2$(dma)Br^{2+}–Hg^{2+} treatment

In addition, retention is established by the isosbestic point data (Table IX) Prior to the isolation of _cis_-[Cr(en)$_2$(dmso)(dmf)] (ClO$_4$)$_2$NO$_3$, some rate data was collected for this species generated from _cis_-Cr(en)$_2$(dmf)Br^{2+} and Hg(dmso)$_6^{2+}$ in DMSO (t$_{1/2}$ < 5 sec under the conditions, Table X) The results are equivalent (470, 480 nm) Note that here, as in all these systems k_{s_2} is not sufficiently small compared to k_{s_1} to enable k_{s_1} to be directly obtained from plots of ln $|D - D_\infty|$ vs time (where D$_\infty$ refers to the mixed solvent species) Also, there are no suitable _cis_-Cr(en)$_2$(dmso)(dmf)$^{3+}$ _cis_-Cr(en)$_2$(dmso)$_2^{3+}$ isosbestic points which would also permit a direct determination of k_{s_1}

Cis-Cr(en)$_2$(dmso)$_2^{3+}$ and -Cr(en)$_2$(dmso)(dmf)$^{3+}$ in DMF

These reactions are the formal reverse of the above but to effect this required a change in solvent No attempts were made to use DMSO/DMF mixtures to bring about a measureable equilibrium which might allow an estimate of the relative ligand strengths of dmso and dmf, severe analytical problems arise Isosbestic point data and the final appearance
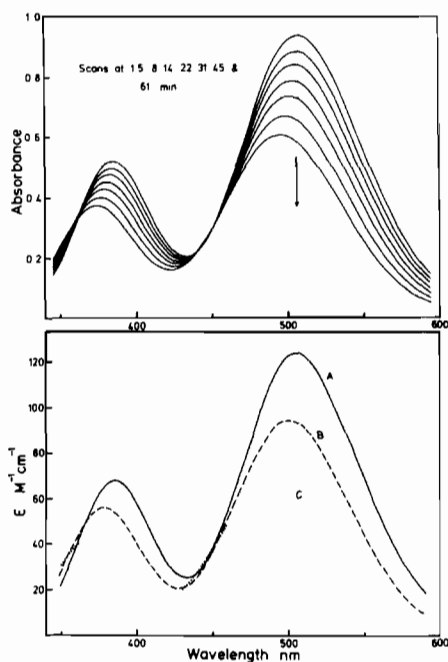

Figure 6 Upper Spectral changes characterizing solvent interchange of _cis_-Cr(en)$_2$(dma)$_2^{3+}$ in 1 0 _M_ HClO$_4$ at 39 0 °C Lower Pure component spectra in 1 0 _M_ HClO$_4$ A, _cis_-Cr(en)$_2$(dma)$_2^{3+}$, B, _cis_-Cr(en)$_2$(dma)OH$_2^{3+}$, C, _cis_-Cr(en)$_2$(OH$_2$)$_2^{3+}$

of _cis_-Cr(en)$_2$(dmf)$_2^{3+}$ assured that both steps in neat DMF were retentive Rate data are given in Table XI k_{s_1} values are not precise because of only slight initial curvature in plots of ln $|D - D_\infty|$ vs time At upper temperatures the plots were close to linear This was traced [32] to the condition (1)

$$\frac{\epsilon_A - \epsilon_C}{\epsilon_B - \epsilon_C} = \frac{k_{s_1}}{k_{s_2} - k_{s_2}} \tag{1}$$

holding,* the plot gives k_{s_2}, and k_{s_1} was estimated using this relation

2 Aquation of Solvento Complexes

Cis-Cr(en)$_2$(dma)$_2^{3+}$ and -Cr(en)$_2$(OH$_2$)(dma)$^{3+}$ in aqueous HClO$_4$

The larger extinction coefficient differences between aqua and analogous solvento species allows greater accuracy in rate data here (Fig 6) The final appearance of the _cis_-diaqua ion together with the isosbestic point data (Table XII) jointly indicate that this stepwise reaction is retentive

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*A, B and C refer to the _bis_(dmso), (dmso)(dmf) and (dmf)$_2$ ions respectively Note that $\Delta H^{\#}$ values for k_{S1} and k_{s_2} must be different since k_{s_1}/k_{s_2} is temperature dependent (ϵ_A, ϵ_B and ϵ_C are not) No suitable wavelength was found which varied the value of $(\epsilon_A - \epsilon_C)/(\epsilon_B - \epsilon_C)$

TABLE XIII. Rate Data[a] for the Reaction: $cis\text{-}Cr(en)_2(dma)(OH_2)^{3+} + OH_2 \rightarrow cis\text{-}Cr(en)_2(OH_2)_2^{3+} + DMA$.

$10^4\ k_{s_2}$, sec^{-1}	$[H^+]$, M	T, °C	$10^4\ k_{s_2}$, sec^{-1}	$[H^+]$, M	T, °C
0.81	0.12	25.0	2.74	0.40	35.3
0.72	0.40	25.1	2.84	0.85	35.4
0.81	0.85	"	2.96	0.12	"
0.69	0.15	"	7.92	0.85	45.0
0.73	0.25	"	7.97	0.40	"
2.63[b]	0.70	35.2	8.13	0.15	"
2.53	0.25	"	8.07	0.12	"
2.53	0.15	"			

[a]Substrate generated by Hg_{aq}^{2+} treatment of bromo complex; $C_0 = (1.39-1.84) \times 10^{-2}\ M$; $[Hg_{aq}^{2+}]_0 = 0.05\ M$; $HClO_4-NaClO_4$ media ($\mu = 1.0$). The k_{s_2} values are from runs at 510 nm. [b]$[Hg_{aq}^{2+}] = 0.10\ M$.

TABLE XIV. Rate Data[a] for the Reaction: $cis\text{-}Cr(en)_2(dma)_2^{3+} \xrightarrow[OH_2]{k_{s1}} cis\text{-}Cr(en)_2(dma)(OH_2)^{3+} + DMA \xrightarrow[OH_2]{k_{s2}} cis\text{-}Cr(en)_2(OH_2)_2^{3+} + 2DMA$.

$10^4\ k_{s1}$, sec^{-1}	$10^4\ k_{s2}$, sec^{-1}	$[H^+]$, M	T, °C
2.42 ± 0.06	1.57 ± 0.04	0.20	29.8
2.50 ± 0.07	1.55 ± 0.06	"	"
2.43 ± 0.09	1.59 ± 0.06	1.0	29.9
4.59 ± 0.05	2.65 ± 0.05	"	35.0
4.46 ± 0.08	2.64 ± 0.08	"	"
7.70 ± 0.20	5.16 ± 0.09	"	40.4
7.46 ± 0.22	5.30 ± 0.12	"	"
7.30 ± 0.21	5.34 ± 0.15	"	"
7.24 ± 0.25	5.57 ± 0.16	"	"

[a]$C_0 = (1.09-1.15) \times 10^{-2}\ M$; $HClO_4$ media ($\mu = 1.0$, $NaClO_4$); The k values are the means of those determined for several ϕ_1, ϕ_2 pairs [32].

Figure 7. Spectral changes characterizing solvent interchange of $cis\text{-}Cr(en)_2(dma)OH_2^{3+}$ generated by using the $cis\text{-}Cr(en)_2(dma)Br^{2+}-Hg_{aq}^{2+}$ treatment (0.25 M $HClO_4$, 0.05 M $[Hg_{aq}^{2+}]_0$, T = 39.5 °C).

Cis-$Cr(en)_2(OH_2)(dma)^{3+}$ was rapidly generated from $cis\text{-}Cr(en)_2(dma)Br^{2+}$ and excess Hg_{aq}^{2+}. k_{s_2} values so obtained (510 nm) are pH independent in the acid range $0.12-0.85M$ $HClO_4$ ($\mu = 1.0$, $NaClO_4$) and are therefore appropriate to aquation. There is also no effect of a two fold change in $[Hg_{aq}^{2+}]_0$ (Table XIII).

k_{s_1} values could not be directly obtained for the $cis\text{-}Cr(en)_2(dma)_2^{3+}$ reactant from plots of $\ln |D - D_\infty|$ *vs.* time which were completely linear. Such linear plots occur under three conditions:

(1) $(\epsilon_A - \epsilon_C)/(\epsilon_B - \epsilon_C) = k_{s_1}/(k_{s_1} - k_{s_2})$,

(2) $\epsilon_B = \epsilon_C$, or

(3) $k_{s_2} \gg k_{s_1}$ [32].

Condition (2) was eliminated since ϵ_B and ϵ_C are known. Again, as earlier, the first condition applies; overlap between the two reaction steps ($k_1 \sim k_2$) is apparent from the steady drift of the 366 nm isosbestic point and the early development of the two points at longer wavelengths (Fig. 6, 7) eliminating condition (3). Thus the slope of the rate plot roughly [32] gives k_{s_2}, already obtained independently
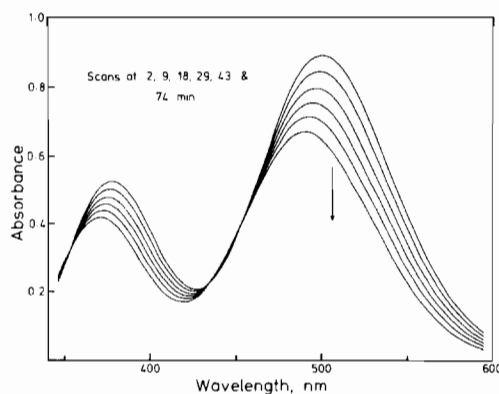
(Table XIII). The system was solved by the more accurate time–ratio procedure; the details and inherent problems are given elsewhere [32]. These results (Table XIV) show that both k_{s_1} and k_{s_2} are acid independent ($0.2-1.0\ MHClO_4$, $\mu = 1.0$, $NaClO_4$).

The isomeric purity of $cis\text{-}Cr(en)_2(OH_2)(dma)^{3+}$ was not established through its isolation as a solid salt, although its spectrum at least suggests predominance of the *cis* form (Fig. 6). Note that kinetic analysis and isosbestic point data establish only that dma aquation in $cis\text{-}Cr(en)_2(dma)_2^{3+}$ and Hg^{2+} promoted Br^- aquation of $cis\text{-}Cr(en)_2(dma)Br^{2+}$ give a common product. However, to argue that some (>5%) *trans* isomer is formed would be to admit the following events: (i) a *cis/trans* ratio that is temperature independent; the present product spectrum (±1%) is not temperature dependent, (ii) *cis*- and *trans*-$Cr(en)_2(OH_2)(dma)^{3+}$ reacting at identical rates (the lengthy proof is not developed here), and (iii) *cis*- and *trans*-$Cr(en)_2(OH_2)(dma)^{3+}$ both aquating to $cis\text{-}Cr(en)_2(OH_2)_2^{3+}$. Moreover, all Hg^{2+} promoted Cr(III) solvolyses reported to date proceed with complete retention.

TABLE XV. Isosbestic Points for the Solvent Interchange of cis-Cr(en)$_2$(dmso)OH$_2^{3+}$ in Perchloric Acid.

Observed λ, nm (ϵ, M^{-1} cm^{-1})	Predicted[a] λ, nm (ϵ, M^{-1} cm^{-1})
578 (39.5)[b]	579 (40.0)
425 (18.1)[b]	426 (18.2)
362 (61.8)[b]	362 (62.2)

[a]Predicted positions assume 100% stereoretention. [b]cis-Cr-(en)$_2$(dmso)(OH$_2$)$^{3+}$ generated by the cis-Cr(en)$_2$(dmso)-Br^{2+}–Hg^{2+} treatment.

Cis-Cr(en)$_2$(dmso)$_2^{3+}$ and -Cr(en)$_2$(OH$_2$)(dmso)$^{3+}$ in aqueous acid

Initial investigations revealed a stepwise and at least predominantly retentive aquation. Again, this reaction conforms to the requirement of a consecutive first order scheme with $k_1 \sim k_2$. However, even time–ratio analyses were frustrated by the considerable errors involved, originating primarily from the small absorbance changes ($\Delta\epsilon \sim 12$ M^{-1} cm^{-1}) and compounded by location of l values [32] near the shallow minima in time–ratio plots.* Trial calculations gave $l = 1 \pm 0.5$ (i.e., 0.5 $k_{s_1} < k_{s_2} < k_{s_1}$), corresponding to 100% variation in k_{s_1} and with a greater uncertainty in k_{s_2}. Further analysis was abandoned; k_{s_2} was obtained separately below.

Details of aquation of cis-Cr(en)$_2$(OH$_2$)(dmso)$^{3+}$ (from cis-Cr(en)$_2$(dmso)Br^{2+} + Hg$_{aq}^{2+}$) are included in Table XV and XVI. To preserve reactant solubility, NO$_3^-$ media were used in place of ClO$_4^-$. Similar comments to the above systems apply here.

Trans-Cr(en)$_2$(dmso)(OH$_2$)$^{3+}$ in HClO$_4$

Three methods were used to generate the reactant: (i) action of Hg$_{aq}^{2+}$ on $trans$-Cr(en)$_2$(dmso)Br^{2+}; (ii)

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*$l = k_{s_2}/k_{s_1}$. Inspection of the typical plot of ref. 32 reveals that large errors in log l come from relatively small uncertainties in log θ^{ϕ_1} − log θ^{ϕ_2}.

action of HClO$_4$ ($2M$) on $trans$-Cr(en)$_2$(dmso)(ONO)$^{2+}$ and (iii) use of the solid triperchlorate in dilute acid. Note that (ii) proceeds without Cr–O fission [33] and therefore with retention. The three approaches gave results in close agreement; moreover, the starting material is assured of being the pure $trans$ isomer.

The typical run (Fig. 8) reveals the complexity of this reaction. Spectral changes fall into two stages, the first and faster involving larger absorbance changes. A single isosbestic point (459 nm) contrasts sharply with the three points (Fig. 8) expected for retentive solvent interchange. The absence of a second isosbestic point above 550 nm excludes any of the possible Cr(en)$_2$ products (or any suitable combination thereof) from explaining these observations. For the second stage isosbestic behaviour vanishes and the spectrum collapses till virtual identity with Cr(en)(OH$_2$)$_4^{3+}$ is obtained (Fig. 8). Absorbance changes at 376, 440 and 500 nm are accurately first order over the first $t_{1/2}$ of the initial reaction, yielding a mean $k_{obs} = (2.6 \pm 0.4) \times 10^{-4}$ sec^{-1} at 25 °C. D$_\infty$ values were taken at 95% completion of the primary step. These data require at least a two step reaction.

The simplest plausible reaction scheme required is:

$$trans\text{-Cr(en)}_2(\text{dmso})(\text{OH}_2)^{3+} \xrightarrow[\text{fast}]{\text{H}_2\text{O},\text{H}^+}$$

$$trans\text{-Cr(en)(eNH)(dmso)(OH}_2)_2^{4+}$$

$$\text{DMSO} + \text{Cr(en)(OH}_2)_4^{3+} \xleftarrow{\text{H}_2\text{O}} \quad \text{slow} \downarrow \text{H}_2\text{O},\text{H}^+$$

$$\text{Cr(en)(dmso)(OH}_2)^{3+} + \text{enH}_2^{2+}$$
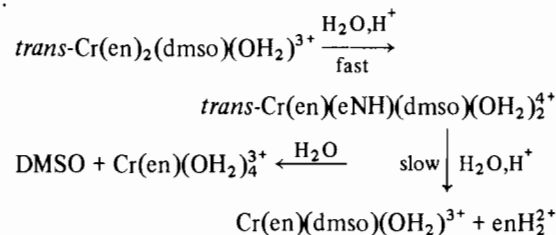
The primary product has not been isolated but its spectrum may be estimated with fair accuracy as follows. The present work has shown the very close similarity in spectra between aqua and dmso analogues; Cr(en)(eNH)(dmso)(OH$_2$)$_2^{4+}$ should be approxi-

#eNH denotes protonated "one-ended" en.

TABLE XVI. Rate Data for the Reaction: cis-Cr(en)$_2$(dmso)OH$_2^{3+}$ + OH$_2 \rightarrow cis$-Cr(en)$_2$(OH$_2$)$_2^{3+}$ + DMSO.

10^4 k_{s_2}, sec^{-1}	[H$^+$], M	T, °C	10^4 k_{s_2}, sec^{-1}	[H$^+$], M	T, °C
2.06	0.40	34.9	3.33	0.40	39.3
2.00	"	"	3.35	"	"
2.15	"	"	6.05[b]	0.75	45.0
2.00	0.85	35.2	6.15	0.85	"
1.98	0.40	35.3	6.27	"	"
2.02	0.25	35.2	5.90	0.25	"
1.85	0.15	"	8.85	"	49.2
1.84	0.12	"	8.95	"	"
			9.15	"	"

[a]Substrate generated by cis-Cr(en)$_2$(dmso)Br^{2+} + Hg$_{aq}^{2+}$ treatment; C$_p$ = (2.40–2.80) $\times$ 10^{-2} M; [Hg$_{aq}^{2+}$]$_0$ = 0.05 M; HNO$_3$ + NaNO$_3$ media (μ = 1.0); k_{s_2} values were from runs at 540 nm. [b][Hg$_{aq}^{2+}$]$_0$ = 0.10 M.

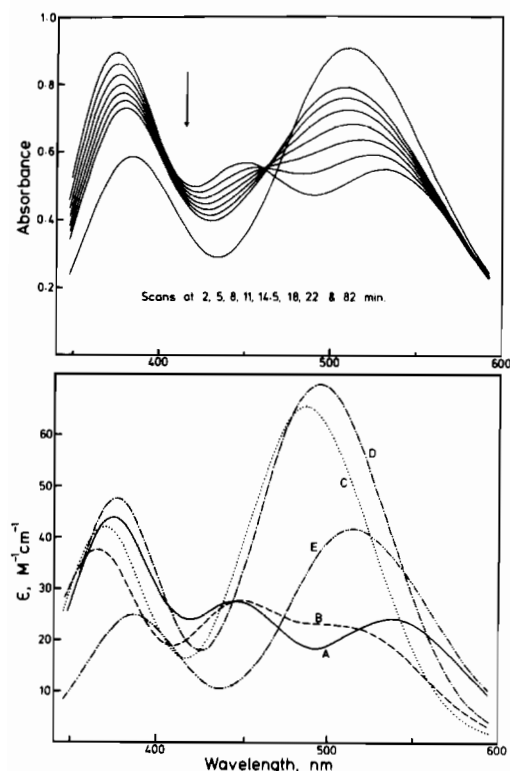Figure 8. Upper: Spectral changes which accompany reaction of *trans*-Cr(en)$_2$(dmso)OH$_2^{3+}$ in dilute HClO$_4$ at 40.1 °C. Lower: Pure component spectra: A, *trans*-Cr(en)$_2$(dmso)-OH$_2^{3+}$; B, *trans*-Cr(en)$_2$(OH$_2$)$_2^{3+}$; C, *cis*-Cr(en)$_2$(OH$_2$)$_2^{3+}$; D, *cis*-Cr(en)$_2$(dmso)OH$_2^{3+}$; E, Cr(en)(OH$_2$)$_4^{3+}$.

mated by Cr(en)(eNH)(OH$_2$)$_3^{4+}$ which in turn should be represented by the average ½ *cis*-Cr(en)$_2$(OH$_2$)$_2^{3+}$ + ½ Cr(en)(CH$_2$)$_4^{3+}$.* The spectrum so obtained (see Fig. 8) has $\epsilon_{calc}^{459} = 29\ M^{-1}\ cm^{-1}$ which agrees closely with $\epsilon_{obs.}^{459} = 27\ M^{-1}\ cm^{-1}$, the reaction isosbestic point. Further, observed extinctions for the primary product at other wavelengths ($\epsilon_{\infty}^{376} = 34\ \epsilon_{\infty}^{440} = 20$, $\epsilon_{\infty}^{500} = 51\ M^{-1}\ cm^{-1}$) agree well with those calculated (32, 18, 53 $M^{-1}\ cm^{-1}$, respectively). However, on this basis alone, we cannot distinguish between the single product Cr(en)(eNH)(dmso)(OH$_2$)$_2^{3+}$ or equimolar mixture of products, *cis*-Cr(en)$_2$(OH$_2$)(dmso)$^{3+}$ and Cr(en)(OH$_2$)$_3$(dmso)$^{3+}$, for the primary reaction step. The sharp isosbestic point requires either a single product, or products formed in constant proportion, consistent with either interpretation. That the product(s) has a CrN$_3$O$_3$ chromophore seems assured.

The spectral behaviour of *trans*-Cr(en)$_2$(dmso)-(OH$_2$)$^{3+}$ remained unchanged over 20–40 °C and the

*The validity of this procedure ("rule of average environment") is discussed elsewhere [9]; *e.g.*, Cr(eNH)(OH)$_5^{4+}$ is accurately an average of Cr(en)(OH$_2$)$_4^{3+}$ and Cr(OH$_2$)$_6^{3+}$ spectra. Similarly for Cr(en)$_2$(sol$_1$)(sol$_2$)$^{3+}$, = ½ (Cr(en)$_2$-(sol$_1$)$_2^{3+}$ and Cr(en)$_2$(sol$_2$)$_2^{3+}$) (this work — see Fig. 4 and 6 and ref. 8).

acidity range 0.01–2.0 M HClO$_4$ (μ = 2.0, NaClO$_4$). The two-hundred fold decrease in acid concentration roughly doubled the value of k$_{obs}$, this increment quite likely arising from a significant rate contribution from the more labile *trans*-hydroxo species. These observations are more consistent with (but do not require) the formation of a single product species.

Discussion

Table XVII summarizes the present results and includes relevant literature data for chromium(III) solvent exchange and interchange. The data are arranged to illustrate the effects of leaving group, non-displaced groups and solvent, where each is now considered in turn.

Leaving Group

The numbers in Table XVII reveal an overall 10^4-fold spread of rate constants. In spite of this there is very little change as a function of the displaced ligand. Except for the anomalously low water exchange coefficient of *cis*-Cr(ox)$_2$(OH$_2$)$_2^-$ (*cf.* rates of anation and isomerization [35]), the k$_s$ values span less than a factor of three for each group of reactions within which only the leaving group is varied. This similarity extends, in most cases, to the activation parameters.

Two interpretations may be adopted. The first assumes a primarily dissociative loss of bound solvent (*d* activation) [36]; the energy required for chromium—solvent rupture is the main component of the activation energy. This mechanism is plausible when it is recognized that essentially the same bond (Cr—O) is broken in each case, although there is little information concerning the relative ligand strengths of the various solvents [37]. The second interpretation assumes that metal—ligand dissociation plays a minor role in determining rate and rate variations reflect solvent effects (*d* activation) or bond making by the incoming nucleophile (*a* activation). Solvent effects are ignored on the grounds that solvation energy changes should be small where neutral leaving groups are involved (variations in this factor from one sol to another should be even less). This supposition seems to hold for correlations of activation volumes, and can be justified further by the lack of solvent dependence on the interchange rates (*vide infra*). The second possibility of nucleophilic assistance cannot be dismissed as readily. Indeed, in view of the evidence for an I$_a$ mechanism in several Cr(III) substitution processes [38] (the water exchange of Cr(OH$_2$)$_6^{3+}$ and Cr(NH$_3$)$_5$(OH$_2$)$^{3+}$ affording pertinent examples) [2, 39], it is an attractive rationale. Thus the absence of a leaving group effect could be construed to reflect the fact that the reactions share a common nucleophile (solvent). If

TABLE XVII. Comparison of Rates and Activation Parameters for Solvent Exchange and Interchange of Some Chromium(III) Complexes.*

Complex	Leaving group	$10^3 k_{25}$,[a] sec^{-1}	$\Delta H^{\ddagger,}$ $kcal\ mol^{-1}$	$\Delta S^{\ddagger}_{25}$ $cal\ deg^{-1}\ mol^{-1}$	Reference
Solvent: DMSO
cis-$Cr(NH_3)_4(OH_2)Cl^{2+}$	OH_2	2.3 ± 0.1	24.0 ± 0.7	0.7 ± 1.5	
cis-$Cr(NH_3)_4(dmf)Cl^{2+}$	dmf	0.86 ± 0.1	22.1 ± 1.5	-8 ± 4	
cis-$Cr(NH_3)_4(dma)Cl^{2+}$	dma	2.5 ± 0.2	22.7 ± 1.4	-4 ± 3	
cis-$Cr(en)_2(OH_2)Cl^{2+}$	OH_2	14.5 ± 0.3	22.1 ± 1	-3 ± 3	
cis-$Cr(en)_2(dmf)Cl^{2+}$	dmf	9.9 ± 0.2	21.5 ± 0.2	-5.5 ± 1.4	
cis-$Cr(en)_2(dma)Cl^{2+}$	dma	10.3 ± 0.4	21.8 ± 0.8	-3.8 ± 1.4	
cis-$Cr(en)_2(dma)_2^{3+}$	dma	62 ± 3	20.5 ± 1	-4.6 ± 3	
cis-$Cr(en)_2(dmso)(dma)^{3+}$	dma	37 ± 1.5^d	19.5 ± 1.2^d	-8.8 ± 2^d	
		41 ± 1.4^e	18.8 ± 1^e	-7.5 ± 2^c	
cis-$Cr(en)_2(dmf)_2^{3+}$	dmf	~ 102	–	–	
cis-$Cr(en)_2(dmso)(dmf)^{3+}$	dmf	33	18.1	-14	
$trans$-$Cr(en)_2(dmf)_2^{3+}$	dmf[f]	$\leqslant 0.2$	–	–	b
$trans$-$Cr(en)_2(dmso)(dmf)^{3+}$	dmf[f]	$\leqslant 0.087$	–	–	b
cis-$Cr(ox)_2(OH_2)_2^-$	OH_2	9.5	28.5	18.9	c
cis-$Cr(ox)_2(dmso)OH_2^-$	OH_2	6.0	29.7	21.9	c
$Cr(dmso)_6^{3+}$	dmso	0.0031	23.3	-15.4	p
Solvent: DMF
cis-$Cr(en)_2(dmf)(dmso)^{3+}$	dmso	28	19.9	-8.0	
cis-$Cr(en)_2(dmso)_2^{3+}$	dmso	~ 42	–	–	
Solvent: H_2O
cis-$Cr(en)_2(dma)_2^{3+}$	dma	8.1 ± 0.7	18.0 ± 2	-17 ± 3	
cis-$Cr(en)_2(dma)OH_2^{3+}$	dma	8.3 ± 0.8^d	21.4 ± 1.8^d	-6.6 ± 3^d	
		7.5 ± 0.7^g	22 ± 2^g	4 ± 4^g	
cis-$Cr(en)_2(dmso)_2^{3+}$	dmso	$\sim 6-12$	–	–	
cis-$Cr(en)_2(dmso)OH_2^{3+}$	dmso	6.1 ± 0.8	20.8 ± 2.5	-8 ± 4	
$trans$-$Cr(en)_2(dmso)OH_2^{3+}$f	dmso	$\leqslant 20$	–	–	
$Cr(NH_3)_5OH_2^{3+}$	OH_2	5.2	25	0	j
$Cr(OH_2)_6^{3+}$	OH_2	0.043	26.2	0.3	k
$Cr(OH_2)_5dmso^{3+}$	dmso	$0.011-0.017$	–	–	l
$Cr(OH_2)_5I^{2+}$h	OH_2	$30-110$	–	–	m
$Cr(OH_2)_5Cl^{2+}$h	OH_2	0.076	–	–	m
$Cr(OH_2)_5X^{2+}$i	OH_2	$0.070-0.074$	–	–	n
(X = Cl, Br, I, NCS)					
cis-$Cr(ox)_2(dmso)_2^-$	dmso	60	12.3	-32	c
cis-$Cr(ox)_2(dmso)OH_2^-$	dmso	30	17.0	-17.6	c
cis-$Cr(ox)_2(OH_2)_2^-$	OH_2	0.39	–	–	o

*Except where noted, data are from this research. Uncertainties in activation parameters are standard deviations from non-linear least squares fit of k_{obs} data to the Absolute Rate Equation. Correction has been made for statistical factors where appropriate. [a]Literature values are those either quoted or calculated from $\Delta H^{\ddagger}$ values and k values given at other temperatures. [b]W. G. Jackson and W. W. Fee, *Inorg. Chem., 14*, 1174 (1975). [c]K. R. Ashley and R. E. Hamm, *Inorg. Chem., 5*, 1645 (1966). [d]Data for the second reaction step of cis-$Cr(en)_2(dma)_2^{3+}$. [e]Data obtained using the isolated salt as the reactant. [f]Uncertain mechanism[b]. [g]Data obtained using the cis-$Cr(en)_2(dma)Br^{2+}$–Hg^{2+}_{aq} treatment to generate the reactant. [h]Data for exchange of *trans* water only. [i]Data for exchange of *cis* water only. [j]T. W. Swaddle and D. R. Stranks, *J. Am. Chem. Soc., 94*, 8357 (1972). [k]D. R. Stranks and T. W. Swaddle, *Inorg. Chem., 93*, 2783 (1971). [l]L. P. Scott, T. J. Weeks, Jr., D. E. Bracken and E. L. King, *J. Am. Chem. Soc., 91*, 5219 (1969). [m]P. Moore, F. Basolo and R. G. Pearson, *Inorg. Chem., 5*, 223 (1966). [n](a) V. Carunchio, G. Illuminati and F. Maspero, *J. Inorg. Nucl. Chem., 28*, 2693 (1966), (b) L. R. Carey, W. E. Jones and T. W. Swaddle, *Inorg. Chem., 10*, 1566 (1971). [o](a) H. Steiger, G. M. Harris and H. Kelm, *Ber. Bunsengesellschaft Phys. Chem., 74*, 262 (1970), (b) J. Aggett, I. Mawston, A. D. Odell and B. E. Smith, *J. Chem. Soc. A*, 1413 (1968). [p]D. L. Carle and T. W. Swaddle, *Can. J. Chem., 51*, 3795 (1973).

TABLE XVIII. Rate Data for Some Aquation Reactions Involving Release of Amine Ligands.

Substrate	$10^9 \, k_N$, sec^{-1}, 25 °C^a	Ref.^{i}
CrO_5N^{n+}		
$Cr(OH_2)_5NH_3^{3+}$	2.0	b
$Cr(OH_2)_5(eNH)^{4+}$	21	c
$Cr(OH_2)_5(dienH_2)^{5+}$	28	d
$Cr(OH_2)_5(trienH_3)^{6+}$	10	e
$Cr(OH_2)_5(tetrenH_4)^{7+}$	8.2	f
$CrO_4N_2^{n+}$		
cis-$Cr(OH_2)_4(NH_3)_2^{3+}$	4.3	b
cis-$Cr(OH_2)_4(en)^{3+}$	10	c
cis-$Cr(OH_2)_4(dienH)^{4+}$	158	d
cis-$Cr(OH_2)_4(trienH_2)^{5+}$	168	e
cis-$Cr(OH_2)_4(tetrenH_3)^{6+}$	43	f
$trans$-$Cr(OH_2)_4(NH_3)_2^{3+}$	26	b
$CrO_3N_3^{n+}$		
fac-$Cr(NH_3)_3(OH_2)_3^{3+}$	5.6	b
mer-$Cr(NH_3)_3(OH_2)_3^{3+}$	37^g	b
	1.6^h	b
$CrO_2N_4^{n+}$		
cis-$Cr(OH_2)_2(NH_3)_4^{3+}$	41^g	b
	5.2^h	b
$trans$-$Cr(OH_2)_2(NH_3)_4^{3+}$	33	b
$CrON_5^{n+}$		
$Cr(OH_2)(NH_3)_5^{3+}$	29^g	b
	<1.5^h	b
CrN_6^{n+}		
$Cr(NH_3)_6^{3+}$	17.6	b

^{a}Corrected for a statistical factor corresponding to the number of equivalent leaving groups. ^{b}L. Mønsted and O. Mønsted, *Acta Chem. Scand.*, *A27*, 2121 (1973); *A28*, 28 (1974); *A28*, 569 (1974). ^{c}R. F. Childers, Jr., K. G. Van der Zyl, Jr., D. A. House and C. S. Garner, *Inorg. Chem.*, 7, 749 (1968). ^{d}D. K. Lin and C. S. Garner, *J. Am. Chem. Soc.*, *91*, 6637 (1969). ^{e}D. A. Kamp. R. L. Wilder, S. C Tang and C. S. Garner, *Inorg. Chem.*, *10*, 1396 (1971). ^{f}S. J. Ranney and C. S. Garner, *Inorg. Chem.*, *10*, 2437 (1971). ^{g}Release of *trans*-NH$_3$. ^{h}Release of *cis*-NH$_3$. $^i\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ or k_T, $\Delta H^{\ddagger}$ data used to obtain k_{25}. ClO$_4^-$ media in all cases (variable ionic strength); NO$_3^-$ "catalysis" of amine release well established (ref. b; T. W. Swaddle *et al.*, *Inorg. Chem.*, *13*, 61 (1974), *Can. J. Chem.*, *52*, 527 (1974).

the degree of bond making remains constant, as seems to be required of $Cr(NH_3)_5X^{n+}$ and $Cr(OH_2)_5X^{n+}$ equations to explain their fit to L.F.E.R. and other kinetic–thermodynamic correlations [40, 41], then variation in the neutral leaving group should have little effect on rate. Although true of sol, processes where the neutral displaced group is a nitrogen donor ligand (Table XVIII) reveal a different story. The

broad trend is for Cr–N cleavage to be less facile than Cr–O cleavage. For instance $Cr(OH_2)_5(amine)^{n+}$ aquation rates are ten to two hundred times slower than $Cr(OH_2)_6^{3+}$ water exchange, while an even larger separation applies to the pentammine system. These data, for reactions with well defined stereochemistry and involving complexes containing only aqua and strain free amine ligands, also illustrate the following points: (i) amine release follows the order NH$_3$ < NH$_2$R < NHR$_2$, reflecting the metal–amine bond strengths. There is no obvious dependence on charge; the site of protonation in the partially "unwrapped" multidentates is remote from the metal ion and the leaving groups are therefore effectively neutral. (ii) amine groups *trans* to a nitrogen donor are activated. This point, very clear in the ammine series, is considered later, and (iii) rates of amine release are insensitive to the nature of the amine and to whether the other donors are oxygen or nitrogen ((i) and (ii) constant). These trends emphasize the bond-breaking aspects of activation; N-donor ligands usually bind more firmly to first row transition elements than do O-donor ligands. Therefore the first interpretation in terms of a common I_d process would seem to best fit both data sets for neutral N- and O-bound leaving groups.

Non-Displaced Groups

Three variables are of concern: one, the effect of chelation; two, substrate charge; and three, substrate geometry.

One

This is seen as a five to tenfold increase between cis-$Cr(NH_3)_4(sol)Cl^{2+}$ and -$Cr(en)_2(sol)Cl^{2+}$ reactivities. Steric acceleration due to bulky amine groups is well documented in Co(III) reactions [1], and here lies an obvious explanation. However, for analogous Cr(III) systems involving anionic leaving groups the extant data reveal little dependence of the rate upon the type of amine ligand [42]. It seems reasonable to conclude that steric factors are not responsible for the observed trends here with Cr(III), particularly since en and NH$_3$ co-ordination should be relatively strain free. A more comprehensive basis for neglecting steric factors is developed elsewhere [43]; the argument links steric acceleration with stereochemical change in substitution. Cr(III), as evidenced in this work, is strictly retentive.

A property which appears to correlate the labilizing power of amine ligands is their ability to reduce d-electron metal ion repulsions — their nephelauxetic effect. It is argued [44] that ligands least able to reduce ground state repulsions will most effectively assist reaction, since greatest benefit derives from electronic delocalization into the empty orbital created in a dissociative transition state; the kinetic and thermodynamic behaviour of many CoN$_4$-

XY^{n+} species have been rationalized thus [44]. If this is true of Cr(III), then the nephelauxetic order en $>$ NH_3 [45] requires the ammine complex to be more reactive. This is contrary to present observations.

Without net charge redistribution during these solvent interchange processes, solvent effects are anticipated to be subtle. Therefore an important consideration is the ease with which solvent can escape the solvent sheath in order to penetrate the co-ordination sphere of the metal ion, in a dissociative reaction. Solvent structuring by simple electrolytes is well developed in DMSO [46]. Thus for cis-$CrN_4(sol)Cl^{2+}$, high dipole moments, high charge and H-donor capacities are particularly conducive to strong solvation [47, 48]. Thus the ion could act as an electrorestrictive "structure-former", i.e., surrounding liquid forms a relatively rigid and firmly held shell, hindering attack at the metal by a solvent molecule. Because of the improved circumstances for H-bond formation and solvation of the amine complexes [48], enhancement of these effects can explain the slower rates.

Two

The present results are seen as further confirmation that complex charge per se has only a minor influence on the replacement of neutral ligands [49–51]. cis-$Cr(en)_2(sol)Cl^{2+}$ react between three to ten times more slowly than $Cr(en)_2(sol)_2^{3+}$. Furthermore this slight retardation by the chloro group stands in sharp contrast with its labilizing effect when the leaving group is anionic [43]. This contrast is informative on two counts: it emphasizes the role of the electrostatic factor in these latter processes, and it points to the fact that the present behaviour is unlikely to result merely from compromize between substrate charge and some other property of varied A.

A more striking instance of charge independence is afforded by the oxalato complexes. These are only slightly more reactive than the bis(en)species, despite a variation in n of four (n = +3 to −1). There is little information as to this effect of ligand modification when the leaving group is anionic [52]; a marked difference in rate is indicated, however.

The greater interchange rates of the bis(solvento) species (over chloro(solvento)) are in keeping with trends in inductive (sol $>$ Cl) and nephelauxetic effects [44], tending to encourage dissociation. The spread of rates for varied sol (non-leaving group) is not unexpectedly small (Table XVII), as has been assumed in earlier considerations of other influence on reactivity. In this regard to cis directing effects, note that labilization by A groups in water exchange of $Cr(OH_2)_5A^{n+}$ (A = OH_2, NCS, Cl, I) is confined to a "trans influence", the exchange rates of the cis waters covering a very narrow range [53, 54].
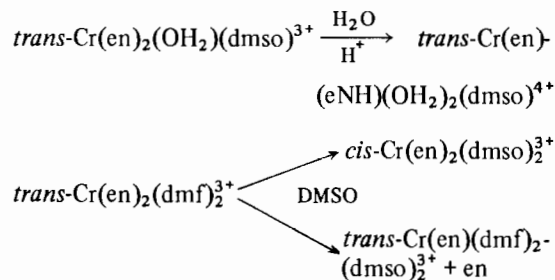
Also here lies a variation in substrate charge, with a (constant) neutral leaving group.

Three

The effect of topology on reactivity has always been recognised as important, but the present data highlight differences in cis/trans lability. The slow and very different reactions of the trans isomers set upper limits for the rates of solvent interchange, limits at least 10^2 times slower than the rates for the cis isomers. This applies to both aqueous and dipolar aprotic media [8].

Differences of this magnitude are difficult to reconcile with solvation or steric effects while the leaving group is neutral, although it has been argued previously that, for anionic leaving groups, solvent transfer from water to dipolar aprotic media enhances the trans to cis reactivity ratio, and this approaches unity in the latter instance [11]. Attention is best directed to some specific displacement property of the trans-bound ligand. Then the greater cis complex reactivity is explained if an $-NH_2$ fragment is more labilizing than a solvent group. There is strong evidence in support of this. Superior accelerating effects of N-donors at Ni(II) and Co(II) centres have been described [50]. For Cr(III), aquations of certain polyamine complexes [55] pass through a sequence of progressively slower steps, displaying a sharpest fall in rate when aquation reaches the step with no remaining trans-amine groups (this parallels acid catalysed aquation behaviour of $Cr(CN)_6^{3-}$ where the C-bound CN group is also apparently trans labilizing [56]. Finally, trans-NH_3 activation is very clearly reflected in the careful kinetic and stereochemical studies of NH_3 aquation in $Cr(NH_3)_n$-$(OH_2)_{6-n}$ [57]. We can now see why the first two dmf ligands in $Cr(en)(dmf)_4^{3+}$ are solvolyzed much more readily than the remaining two in DMSO [8], if the "equatorial" (trans-N) ligands are lost first [8].

To consider alone the reactions of the trans isomers we must digress from solvent interchange. The major reaction is isomerization and parallel loss of amine. Here aqueous and dipolar aprotic media [8] afford a contrast, e.g.,

trans-$Cr(en)_2(OH_2)(dmso)^{3+}$ $\xrightarrow[\text{H}^+]{\text{H}_2\text{O}}$ trans-Cr(en)-(eNH)(OH$_2$)$_2$(dmso)$^{4+}$

trans-$Cr(en)_2(dmf)_2^{3+}$ $\Big\langle$ $\xrightarrow{}$ cis-$Cr(en)_2(dmso)_2^{3+}$ DMSO $\searrow$ trans-Cr(en)(dmf)$_2$-(dmso)$_2^{3+}$ + en

The major difference is the appearance of isomerized reactant (~85%) in the first formed products in DMSO, and no $Cr(en)(eN)(dmf)_2(dmso)^{3+}$. This was

rationalized previously by assuming its rate determining formation followed by a more rapid decay; Cr-eN cleavage to $Cr(en)(dmf)_2(dmso)_2^{3+}$, or rechelation to *cis*- and *trans*-$Cr(en)_2(dmf)_2^{3+}$; *cis*-$Cr(en)_2(dmf)_2^{3+}$ leads to *cis*-$Cr(en)_2(dmso)_2^{3+}$ "instantly" [8]. The rechelation of Cr-eN was proposed to explain the non-accumulation of the eN species, confirmed by acid quenching [8], and it was suggested but not demonstrated that isomerization could proceed this way. The present although limited work on *trans*-$Cr(en)_2(OH_2)(dmso)^{3+}$ supports these suggestions, where it is apparent that the only initial reaction is en aquation (chelate opening), followed more slowly by its complete loss (together with concurrent dmso aquation). Note that an analogy is seen in en aquation [58] of *trans*-$Cr(en)_2F_2^+$; the earlier assertion that the first formed *trans*-$Cr(en)(enH)$-$(OH_2)F_2^{2+}$ slowly isomerized to *cis*-$Cr(en)_2(OH_2)F^{2+}$ by rechelation in acid medium has been rebuked by later work [59]; it aquates to *trans*-$Cr(en)(eNH)$-$(OH_2)_2F^{3+}$.

Solvent

Although strictly the reaction of only three complexes was examined as a function of solvent, it is reasonable to compare collectively data for the *bis*-(solvento) *cis* species. Accordingly, the suggested trend in solvent activity is DMSO > DMF ~ H_2O, albeit with a total spread of rates of no more than about an order of magnitude.

This small variation conjures two points. Firstly, it contrasts with the marked solvent sensitivity where the leaving group is anionic (*e.g.*, *cis*-$Cr(en)_2Br_2^+$ H_2O >> DMSO > H_2O, 94:2:1, 25 °C; *cis*-$Cr(en)_2$-Cl_2^+ 300:3:1) [11]. The sharp acceleration on transfer from dipolar aprotic solvents to water stems chiefly from the vastly improved anion solvation, a major driving force in dissociative aquation [11]. Clearly solvation effects are not nearly as important when the displaced group is a neutral solvent molecule.

The second aspect concerns the role of nucleophilic assistance. An argument maintaining an I_d mechanism solely on the basis of the reagent independence of rates must remain weak in the absence of a reliable guide to solvent nucleophilicity. The scale DMSO > DMF > H_2O appears to hold for Pt(II) substitution [60]; it is doubtful whether this applies also to Cr(III) reactions, but it seems pertinent to note that DMSO probably binds initially through the more nucleophilic S in I_a ractions (*cf.* S bonding of NCS⁻ scavenging $Co(NH_3)_5^{3+}$ [61]. No evidence for S-bonded DMSO (or N-bonded DMF, DMA) was found in this or our previous work.

Finally, we note that the lack of solvent dependence of solvent interchange rates, coupled with the small leaving group effects, allows an estimate of Cr(III) solvent exchange rates. For example, the *cis*-$Cr(en)_2(dmf)(dmso)^{3+}$ in DMF

and *cis*-$Cr(en)_2(dmso)(dmf)^{3+}$ in DMSO rates are both ~3×10^{-4} sec⁻¹ at 25 °C, which is probably close to the *cis*-$Cr(en)_2(dmf)_2^{3+}$/DMF and *cis*-Cr-$(en)_2(dmso)_2^{3+}$/DMSO exchange rates. This correlation is less reliable for Co(III) [7], although interestingly H_2O exchange in *cis*-$Co(en)_2(OH_2)_2^{3+}$ [4] and DMSO exchange in *cis*-$Co(en)_2(dmso)_2^{3+}$ [6, 7] both proceed at the same rate (~8.3×10^{-5} sec⁻¹, 35 °C). However for Co(III), the activation energies are more leaving group sensitive [7]. In water, mechanistic information has been derived from the relation between exchange and anation rates [5, 36]. Exchange rates for *cis*-$Cr(en)_2(dmf)_2^{3+}$ and *cis*-Cr-$(en)_2(dmso)_2^{3+}$ deduced from this work indicate that both Cl⁻ and Br⁻ anation [62, 63] proceed much more slowly (½ to 1/50th the solvent exchange rate at 25 °C and under conditions of at least complete ion pair and probably ion triplet formation). While this might be construed as indicating I_d anation mechanisms, the overwhelming effects of ion association in significantly modifying both ground and transition state free energies renders such conclusions doubtful [64].

Finally, brief mention should be made of the insignificant influence of bromide and nitrate ion on the solvent interchange reactions. The apparent indifference to ion association is in line with behaviour of allied systems [7, 62]. This behaviour can be related to the absence of charge effects since the kinetic consequences of ion association appear to be largely electrostatic in origin.

Conclusion

The study of solvent interchange rates of CrN_4A-$(sol)^{n+}$ complexes has not permitted an unambiguous or even a common mechanism assignment. However an I_d process best fits all the results, including previous data on neutral amine leaving groups. The normally subtler effects in influencing the rates of substitution have been more exposed by the restriction to uncharged solvent leaving groups. Thus, for example, it is now apparent that there is an inherent *cis/trans* reactivity difference in $Cr(en)_2AX^{n+}$ (*cis* >> *trans*), at least where A is a neutral oxygen donor. Also, the marked reactivity difference seen between $Co(NH_3)_4$ and chelate complexes *e.g.*, $Co(en)_2$, does not exist with Cr(III) analogues, and the explanation would seem to lie in the different solvation changes accompanying dissociation. Connected with this Co(III) undergoes ready steric rearrangement, in contrast to Cr(III).

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