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Aquation of *Trans*-Chloro(dimethylsulfoxide)bis(ethylenediamine)cobalt(III)

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The trans$[Co(en)_2(OSMe_2)Cl]^{2+}$ *ion aquates rapidly at 25 °C in 0.1 mol* dm^{-3} $HClO_4$; $k_a = (8.7 \pm 0.4)\ 10^{-4}\ s^{-1}$. *The steric course for the loss of* Me_2SO *has been precisely determined by spectrophotometry, 70.5 ± 1.5%* trans *product. The release of* Cl^- *is not a competitive reaction. Subsequent to aquation the* $[Co(en)_2(OH_2)Cl]^{2+}$ *isomers interconvert;* $k_i = (9.90 \pm 0.16)\ 10^{-5}\ s^{-1}$, *79 ± 1%* cis *at equilibrium. These results agree with those obtained independently for* cis- *and* trans$[Co(en)_2(OH_2)Cl]S_2O_6 \cdot H_2O$; $k_i = (10.4 \pm 0.2)\ 10^{-5}\ s^{-1}$, *79 ± 1%* cis. *The steric course of the very rapid chlorine induced aquation of* trans$[Co(en)_2(OSMe_2)Cl]^{2+}$ *has been determined under the same conditions; 69.5 ± 0.5%* trans-$[Co(en)_2(OH_2)Cl]^{2+}$ *product. The common stereochemistry of aquation for these and related reactions is discussed. It is concluded that all the aquations are dissociative and that a reactive common pentacoordinate intermediate is involved.*

Introduction

The determination of the steric course of spontaneous and induced aquation of $[Co(en)_2AX]^{n+}$ complexes has received close attention in recent years [1–3]. This type of study has a history of errors and the recent emphasis has been on lending credibility to the results by defining the steric course more accurately than before. Thus, for example, the resolved *cis* isomers have been examined both polarimetrically and spectrophotometrically to afford independent probes on the steric course [1, 4]. Since the dependence of the steric course on the nature of the leaving group X is important in considerations on mechanism [5], there have been efforts also to extend the range of leaving groups.

The rates and steric course of spontaneous aquation of *cis*$[Co(en)_2(sol)Cl]^{2+}$ (sol = dimethylformamide, Me_2SO and dimethylacetamide) [6] and the steric course of Cl_2 induced aquation of (+)*cis*$[Co(en)_2(Me_2SO)Cl]^{2+}$ have been examined and a common result for the loss of Me_2SO found [1]. These were important results because Me_2SO and Me_2SO_2-(Cl_2 + Me_2SO) as leaving groups represented variations in formal charge and reactivity, both of which were believed to be important in determining mechanism.

The *trans*$[Co(en)_2AX]^{n+}$ ions have not received the same close attention as the *cis* and a need has arisen to examine these. This need is accentuated by the leaving group independence of the steric course for the *cis* complexes which indicates five coordinate intermediates [1] but which conflicts with data for related systems [7]. We were prompted therefore by the recent synthesis of the elusive *trans*$[Co(en)_2(Me_2SO)Cl]^{2+}$ ion [8] to determine the steric course of the spontaneous and Cl_2 induced aquation for comparison with the analogous reactions of the *cis* isomer, and these are now reported.

Experimental

Visible spectra were measured on a Cary 1180 spectrophotometer with a cell block thermostated to 25.0 ± 0.05 °C [8]. Perchloric acid (AnalaR) and redistilled trifluoromethane-sulfonic acid ("Fluorochemical acid", MMM Co.) were standardized against NaOH (Volucon). The complexes *trans*$[Co(en)_2(Me_2SO)Cl]S_2O_6$, *trans*$[Co(en)_2(Me_2SO)Cl](ClO_4)_2$ and *trans*$[Co(en)_2(OH_2)Cl]S_2O_6 \cdot H_2O$ were from fresh batches of fully characterized samples used for concurrent work [8, 9]. *Cis*$[Co(en)_2(OH_2)Cl]Br_2 \cdot H_2O$ and *cis*$[Co(en)_2(OH_2)Cl]SO_4 \cdot 2H_2O$ were obtained as previously described [1]. The bromide salt recrystallized from water using $LiNO_3$ and $LiClO_4 \cdot 3H_2O$ gave the known [10] *cis*$[Co(en)_2(OH_2)Cl]BrNO_3$ rather than *cis*$[Co(en)_2(OH_2)Cl]NO_3 \cdot ClO_4$ as reported [11]. The new salt *cis*-$[Co(en)_2(OH_2)Cl]S_2O_6 \cdot H_2O$ was prepared by the addition of $Li_2S_2O_6$ to a saturated solution of the dibromide, and was recrystallized from water (pH3, 5 °C) using a third volume of cold saturated aqueous $Li_2S_2O_6$ to afford pink needles of the monohydrate (vacuum dried, P_2O_5). *Anal.* Calcd. for $[Co(en)_2(OH_2)Cl]S_2O_6 \cdot H_2O$: C, 11.7; H, 4.91; N, 13.6, S, 15.6; Cl, 8.63. Found: C, 11.8; H, 4.7; N, 13.5; S, 15 7, Cl, 8 66 The *cis* salts were recrystallized to a constant and common absorption spectrum (ϵ, ±0 5%) to guarantee the isomeric purity (ϵ_{517}^{max} 87 4, ϵ_{434}^{min} 16 5, ϵ_{374}^{max} 72 2, ϵ_{335}^{min} 34 1 mol^{-1} dm^3 cm^{-1}, 0 1 mol dm^{-3} $HClO_4$)

The rates of isomerization of *cis*- and *trans*$[Co(en)_2(OH_2)Cl]S_2O_6 \cdot H_2O$ and aquation of *trans*-$[Co(en)_2(Me_2SO)Cl](ClO_4)_2$ were determined spectrophotometrically at 25 °C The spectra of reacting solutions were scanned in the range 650–340 nm to locate the isosbestic points The isomerization reaction was followed in 0 01, 0 1 and 1 0 mol dm^{-3} $HClO_4$ as well as in the 0 1 mol $dm^{-3}$$CF_3SO_3H$, the aquation in 0 1 mol dm^{-3} $HClO_4$ only First order rate constants k_1 for the isomerization reaction were determined by the Guggenheim method [12] or from plots of ln (A_∞ – A) *vs* t which were linear over at least $3t_{1/2}$ Most data were obtained at 510 nm where absorbance changes are greatest (ϵ_{510}(*trans*) = 9 6, ϵ_{510}(*cis*) = 86 3) Infinite time spectra were recorded also for the dibromide, bromide nitrate and sulfate salts of *cis*$[Co(en)_2(OH_2)Cl]^{2+}$ in 0 1 mol dm^{-3} $HClO_4$

The reaction of *trans*$[Co(en)_2(Me_2SO)Cl]^{2+}$ (A) was found to occur stepwise, first with loss of Me_2SO to give $[Co(en)_2(OH_2)Cl]^{2+}$ (B) of a particular *cis*/*trans* composition, followed by *trans* to *cis* isomerization to a mixture (C) of a different composition Conventional analyses [1, 13] for a $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ reaction scheme were applied to obtain k_1, k_2 and the isomeric composition of B Plots of ln(A_C – A) *vs* t were made from the data in the form of continuous A *vs* t traces and at 510 nm they showed the typical [13] marked initial curvature followed by a linear section The data were easily resolved graphically into two first order processes, 10^4 k_1 = 8 7 ± 0 4(3) and 10^5 k_2 = 9 9_0 ± 0 1_6(3)* s^{-1} Although $k_1 \cong 10 k_2$ it was not possible to directly and accurately measure the spectrum of the first formed product mixture B because at completion of the k_1 reaction ($10t_{1/2}$), the extent of subsequent isomerization was significant (~55%) However the extrapolation of the linear segment of ln (A_C – A) *vs* t plots to t = 0 gives [13] an intercept ln[$(A_B - A_C)k_1/(k_2 - k_1)$] from which A_B and hence ϵ_B can be calculated precisely using the measured final absorbance A_C and the known values of [Co], k_1 and k_2 The steric course was calculated from the ϵ_B values (32 0 ± 1 0(3)) using the relation

$$\%\ \textit{trans}\ \text{product} = 10^2(\epsilon_B - \epsilon_{cis})/(\epsilon_{trans} - \epsilon_{cis}) =$$

$$= 70\ 7 \pm 1\ 5$$

A similar result was obtained (ϵ_B = 32 5 ± 1 0(3), % *trans* = 70 ± 1 5) from the expression

$$A - A_C =$$

$$[(A_A - A_C) + k_1(A_B - A_C)/(k_2 - k_1)]e^{-k_1t} -$$

$$- [k_1(A_B - A_C)/(k_2 - k_1)]e^{-k_2t}$$

This is done with maximum accuracy [13] using the measured A, t at the time corresponding to the maximum concentration of B (t_{Bmax} = [ln(k_2/k_1)]($k_2 - k_1$) = 2819 s) Note that in both these calculations the term $1/(k_2/k_1 - 1)$ appears and because $k_2 \cong 0\ 1\ k_1$ the ϵ_B result is not sensitive to errors in k_1 and k_2

The steric course of Cl_2 induced aquation of *trans*$[Co(en)_2(Me_2SO)Cl]^{2+}$ was determined from the product $[Co(en)_2(OH_2)Cl]^{2+}$ spectrum corrected for subsequent isomerization, as described for the *cis* isomer [1,2] Weighed complex samples were dissolved directly in 1 0 mol dm^{-3} $HClO_4$ saturated with Cl_2 (~0 08 mol dm^{-3}), or 0 10 mol dm^{-3} $HClO_4$ where [Cl_2] = 0 02 or 0.08 mol dm^{-3} at 25 °C The extinction coefficient of the product was measured at 510 nm, as well as at one of the *cis*/*trans*$[Co(en)_2(OH_2)Cl]^{2+}$ isosbestic points ($\epsilon_{586\ 5}$ 31 0) to check on the completeness of reaction and for products other than $[Co(en)_2(OH_2)Cl]^{2+}$ None were found The Cl_2 oxidation reactions were complete within 1–2 min

Results and Discussion

Isomerization

The *trans* ⇄ *cis*$[Co(en)_2(OH_2)Cl]^{2+}$ rates were required to determine the steric course of aquation of *trans*$[Co(en)_2(Me_2SO)Cl]^{2+}$ under identical conditions (0 1 mol dm^{-3} $HClO_4$, see below) They have been measured previously in 0 01 mol dm^{-3} $HClO_4$ [14] and 0 01 mol dm^{-3} HNO_3 [15] using $[Co(en)_2(OH_2)Cl]SO_4$ salts Also, it has been shown that the rates and equilibrium position for the analogous *trans* ⇄ *cis*$[Co(en)_2(OH_2)N_3]^{2+}$ isomerization differ significantly in SO_4^{2-} compared with ClO_4^- or $S_2O_6^{2-}$ media [1] Therefore the chloroaqua system was reexamined using the non-coordinating $S_2O_6^{2-}$ salts

Sharp isosbestic points in the expected positions endured for the entire (up to 20 $t_{1/2}$) *trans*- to *cis*- and *cis*- to *trans*$[Co(en)_2(OH_2)Cl]^{2+}$ isomerization reaction (Table I) Commencing with either isomer, final spectra corresponded to a mixture of 79 ± 1% *cis*, 21 ± 1% *trans* at all wavelengths in the range 650–340 nm The previous result was 73 ± 0 5% *cis* [14]; the difference lies largely in the extinction coefficients of the pure *cis* and *trans* isomers used

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*Mean and standard deviation, throughout ( ) denotes the number of determinations

TABLE I. Visible Absorption Spectral Data for Some Cobalt(III) Complexes in 0.1 mol dm^{-3} $HClO_4$ at 25 °C.

		$\epsilon_{586.5}$	ϵ_{582}	ϵ_{510}	$\epsilon_{456.5}$	$\epsilon_{455.5}$	ϵ_{409}	ϵ_{401}	ϵ_{367}	ϵ_{356}
trans$[Co(en)_2(OH_2)Cl]S_2O_6 \cdot H_2O$	t = 0	31.0[a]	30.8	9.6	28.1[a]	28.7	34.9[a]	39.1	52.7	56.2[a]
	$10t_{1/2}$[b]			69.8						
	$20t_{1/2}$[b]			69.5						
cis$[Co(en)_2(OH_2)Cl]S_2O_6 \cdot H_2O$	t = 0	30.7[a]	34.3	86.3	27.6[a]	26.1	34.3[a]	45.8	69.3	57.1[a]
	$10t_{1/2}$[b]			71.0						
trans$[Co(en)_2(Me_2SO)Cl](ClO_4)_2$	t = 0		31.5[c]	7.0		28.0[c]		40.6[c]	57.5[c]	
	$15t_{1/2}$[b]			70.4						
	ϵ_{isos} (calc)[d]		31.9			27.9		41.1	57.7	

[a] Observed isosbestic points for isomerization of $[Co(en)_2(OH_2)Cl]^{2+}$. [b] $t_{1/2}$ = half-life of rate of approach to equilibrium for *trans* ⇄ *cis*$[Co(en)_2(OH_2)Cl]^{2+}$. [c] Observed isosbestic points for aquation of *trans*$[Co(en)_2(Me_2SO)Cl^{2+}$. [d] Calculated for 70.0% *trans*, 30.0% *cis*$[Co(en)_2(OH_2)Cl^{2+}$ first formed product.

TABLE II. Rate Constants for $[Co(en)_2(OH_2)Cl]^{2+}$ Isomerization at 25.0 °C.

$$trans \underset{k_{ct}}{\overset{k_{tc}}{\rightleftarrows}} cis$$

	10^5 k_i, s^{-1} [a,b]	10^5 k_i (av), s^{-1} [c]	10^5 k_{tt}, s^{-1} [d]	10^5 k_{ct}, s^{-1} [d]
0.01 mol dm^{-3} $HClO_4$	1.07, 1.10, 1.08	10.8	8.5	2.3
0.10 mol dm^{-3} $HClO_4$	1.04, 1.05, 1.03	10.4	8.2	2.2
0.10 mol dm^{-3} CF_3SO_3H	1.02, 1.00, 1.03	10.2	8.0_5	2.1_5
1.00 mol dm^{-3} $HClO_4$	1.11, 1.12, 1.09	11.0	8.7	2.3
0.01 mol dm^{-3} $HClO_4$		9.4[e]	6.8_5[e]	2.5_5[e]
0.01 mol dm^{-3} HNO_3		9.7[f]	7.1[f]	2.6[f]
0.10 mol dm^{-3} $HClO_4$	9.7_7, 9.8_6, 10.0	9.9[g]	7.8[g]	2.1[g]

[a] [Co], 5×10^{-3}–5×10^{-2} mol dm^{-3}. [b] $k_i = k_{tt} + k_{tc}$; each entry represents a separate measurement. [c] Mean value; ±2% (this work). [d] Calculated from k_i and measured equilibrium position (79.0% *cis*); *i.e.*, $k_{tt}/(k_{tt} + k_{tc}) = 0.79_0$. [e] Previous values; M. E. Baldwin, S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 4637 (1961). [f] Previous values; A. M. Sargeson, *Aust. J. Chem.*, *16*, 352 (1963). [g] Value obtained for isomerization following *trans*$[Co(en)_2(Me_2SO)Cl]^{2+}$ aquation (refer to text).

in the calculation. Equilibrated solutions of *cis*$[Co(en)_2(OH_2)Cl]SO_4 \cdot 2H_2O$, $[Co(en)_2(OH_2)Cl]Br_2 \cdot H_2O$ and $[Co(en)_2(OH_2)Cl]BrNO_3$ gave the same result (79%) calculated at 510 nm (ϵ 70.5); however at lower wavelengths (~350 nm) ϵ values were significantly higher than expected and indicative of a little Br^- or NO_3^- coordination. Under the conditions ($[HClO_4]$ = 0.1 mol dm^{-3}; [Co] = (5–10) $\times$ 10^{-3} mol dm^{-3}) sulfate coordination was not observed. The rate data are given in Table II and it is clear that the nature of the anion ($S_2O_6^{2-}$, HSO_4^-, ClO_4^- $CF_3SO_3^-$) and ionic strength (μ = 0.01–1.0 mol dm^{-3}) are not important. The present results although perhaps more precise do not differ substantially from the previous data. The main difference lies in the k_{tt} values which in turn arise from the revised value for the equilibrium position. We confirm the occurrence of irreversible Cl^- loss ($t_{1/2}$ ~ 241 h, 25 °C) [16] from $[Co(en)_2(OH_2)Cl]^{2+}$ at long reaction times (>$20t_{1/2}$, k_i).

Spontaneous and Induced Aquation of trans$[Co(en)_2(Me_2SO)Cl]^{2+}$

The spontaneous reaction occurs stepwise:

trans$[Co(en)_2(Me_2SO)Cl]^{2+}$

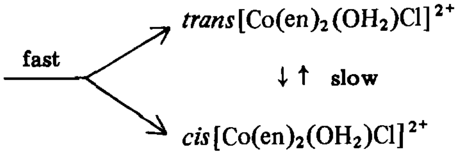

TABLE III. Steric Course of Spontaneous and Induced Aquation of *trans*$[Co(en)_2ClX]^{n+}$.

Reactant	Aquation Mode	% *trans* product
trans$[Co(en)_2Cl(Me_2SO)]^{2+}$	spontaneous	70.5 ± 1.5[a]
trans$[Co(en)_2Cl(Me_2SO)]^{2+}$	Cl_2 induced	69.5 ± 1.0[a]
trans$[Co(en)_2Cl_2]^+$	spontaneous	65 ± 5[b]
trans$[Co(en)_2Cl_2]^+$	Hg^{2+} induced	72 ± 5[c]
trans$[Co(en)_2ClN_3]^+$	NO^+ induced	73.0 ± 0.5[d]

[a] This work, 0.1 *M* $HClO_4$, 25 °C. [b] M. E. Baldwin, S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 4637 (1961). [c] 0.5 *M* H_2SO_4, 20 °C; A. M. Sargeson, *Aust. J. Chem.*, *17*, 385 (1964). [d] W. G. Jackson, *Inorg. Chim. Acta*, *10*, 51 (1974).

Sharp isosbestic points were observed for the initial faster reaction but except for ϵ_{367} these were not diagnostic of the steric course (Table I). However, despite the similarity of the *trans*$[Co(en)_2(Me_2SO)Cl]^{2+}$ and *trans*$[Co(en)_2(OH_2)Cl]^{2+}$ spectra, the steric course was accurately defined by following the stepwise reaction at 510 nm and calculating the extinction coefficient for the first formed product as described previously [1]. The observed isosbestic points are consistent with those calculated using this result (ϵ_{510} = 32.0, % *trans* product = 70.5) and the spectrum of the final product was identical to that obtained commencing with either *cis*- or *trans*$[Co(en)_2(OH_2)Cl]^{2+}$ (Table I). Therefore the substitution of Me_2SO by H_2O is complete and loss of Cl^- is not a significant side reaction.

The rate constant for aquation was measured as $(8.7 \pm 0.4) \times 10^{-4}$ s^{-1} ($t_{1/2}$ ~ 13 min; 0.10 mol dm^{-3} $HClO_4$, 25 °C). The rate constant for the subsequent $[Co(en)_2(OH_2)Cl]^{2+}$ isomerization reaction under the same conditions was found to be $(9.9_0 \pm 0.1_6^6) \times 10^{-5}$ s^{-1}, which agrees very well with the independently determined value, $(10.4 \pm 0.2) \times 10^{-5}$ s^{-1}, (Table II). This confirms the fast–slow assignment of rate constants k_1, k_2 in the analysis of the consecutive processes [13].

These results may be compared with those for the spontaneous aquation of the *cis* isomer [6]. It aquates with loss of Me_2SO much more slowly than the *trans* form ($k = 1.5 \times 10^{-5}$ s^{-1}; ~60 fold less reactive), and Cl^- loss is an important side reaction. In the context of relative *trans*/*cis* reactivity, it is noted that *cis*$[Co(en)_2Cl_2]^+$ or *cis*$[Co(en)_2ClBr]^+$ is more reactive (~10-fold) than its *trans* isomer, for loss of Cl^- or Br^-, while this work has shown that the reverse is true for the neutral leaving group Me_2SO. Also, for the *cis* complexes $[Co(en)_2N_3X]^{n+}$, $[Co(en)_2NO_2X]^{n+}$ and $[Co(en)_2(NCS)X]^{n+}$, rates of aquation [2, 17] at 25 °C indicate that Cl^- is similar to Me_2SO as a leaving group whereas for the *trans* isomers Me_2SO is superior to Cl^-. The labilizing effect of the A group in $[Co(en)_2AX]^{n+}$ complex aquation reactions has been inferred from data very largely pertaining to Cl^- and to a lesser extent Br^- as leaving groups [18], and the above examples are given to show that such interferences from limited leaving group data can be very misleading. Clealry, the effects on hydrolysis rates of the 'orientating' [19] group A and leaving group X are not independent. The duality of the mechanism [19] for $[Co(en)_2AX]^{n+}$ aquation was originally proposed on the basis of the effect of the A group on Cl^- hydrolysis rates. Although it has been long since rejected on other grounds [17], it is clear now its basis was ill-founded.

The chlorine oxidation of *trans*$[Co(en)_2(Me_2SO)Cl]^{2+}$ gave ϵ_{510} 33.0 ± 0.4, corresponding to 69.5 ± 1.0% *trans*$[Co(en)_2(OH_2)Cl]^{2+}$ at 25 °C in 0.1 mol dm^{-3} $HClO_4$. Less *trans* (62.0 ± 1.0%) is produced in 1 mol dm^{-3} $HClO_4$ (ϵ_{510} 38.9 ± 0.4(3)). Differences were found for the perchlorate (ϵ_{510} 36. 5 ± 0.4(3)) and dithionate salts (ϵ_{510} 38.9 ± 0.4(3)) in 1.0 mol dm^{-3} but not 0.1 mol dm^{-3} $HClO_4$. These results were independent of $[Cl_2]$ (0.02–0.08 mol dm^{-3}) which was always in excess and the differences are attributed to technique. In 1 *M* $HClO_4$ the rate of Cl_2 oxidation was faster than the rate of dissolution of the perchlorate but not the dithionate salt. In 0.1 mol dm^{-3} $HClO_4$, both salts could be dissolved completely before significant oxidation. The result for the heterogeneous reaction is therefore considered spurious. Similar small but real differences in the apparent steric course between homogeneous and heterogeneous induced aquation have been found previously [16].

The present and previous steric course results for spontaneous and induced aquation of *trans*$[Co(en)_2ClX]^{n+}$ in 0.1 mol dm^{-3} $HClO_4$ at 25 °C are summarized in Table III. It is apparent that all the induced aquations give a product proportion which is independent of the leaving group. The results for the spontaneous aquation of *trans*$[Co(en)_2Cl_2]^+$ although similar is not as precise (±5%), and hence the corresponding result for *trans*$[Co(en)_2(Me_2SO)Cl]^{2+}$ (±1.5%) is an important addition to these data since it indicates that spontaneous aquation follows the same trend. The complexes vary widely in reactivity and the leaving groups differ in formal charge, size and bonding geometry and on this basis the evidence for a common reduced coordination number is reasonable.

This account is in line with that for the corresponding reactions of the *cis* isomers [1, 2], albeit some of the steric course data for the *trans* reactions are less precise. Experiments are in progress [17] to improve the precision under unified reaction conditions. At the very least, the insensitivity of the steric course to the nature of the leaving group X indicates that the metal–X bond is largely if not entirely broken at the first transition state for aquation, *i.e.*, the mechanism for all these reactions is essentially dissociative.

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