Cleavage of Di-μ-hydroxo-bis-[bis(ethylenediamine)chromium(III)] in Hydrochloric Acid and Characterization of the Monohydroxo-Bridged Intermediates Containing Coordinated Chloride

Johan Springborg

Chemistry Department, Royal Veterinary and Agricultural University, Thorvaldsensvej 40, DK-1871 Frederiksberg C, Denmark

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The cleavage of Δ,Λ-$(en)_2Cr(OH)_2Cr(en)_2^{4+}$ in 12 M HCl (1.0 °C) has been studied spectrophotometrically and by cation-exchange chromatography. The reaction leads to a mixture of cis-$Cr(en)_2(H_2O)_2^{3+}$ (43 %), cis-$Cr(en)_2(H_2O)Cl^{2+}$ (19 %) and cis-$Cr(en)_2Cl_2^+$ (38 %), and it involves a series of consecutive and parallel reactions. The first bridge cleavage yields $\Delta,\Lambda/\Lambda,\Delta$-$Cl(en)_2Cr(OH)Cr(en)_2(H_2O)^{4+}$, which then undergoes direct bridge cleavage by aquation, and by anation and bridge cleavage via Δ,Λ-$Cl(en)_2Cr(OH)Cr(en)_2Cl^{3+}$. It is shown that the last-mentioned reaction path makes a contribution of 0–13 % to the entire reaction, and the pseudo first-order rate constants for each of the cleavage reactions, based upon these limiting values, have been determined.

The first intermediate, i.e. $\Delta,\Lambda/\Lambda,\Delta$-$Cl(en)_2Cr(OH)Cr(en)_2(H_2O)^{4+}$, has been characterized in solution by its absorption spectrum. The second intermediate, Δ,Λ-$Cl(en)_2Cr(OH)Cr(en)_2Cl^{3+}$, has been isolated as a crystalline, stable chloride perchlorate salt from the reaction of Δ,Λ-$(en)_2Cr(OH)_2Cr(en)_2^{4+}$ in 0.5 M HCl, 0.5 M LiCl. Kinetic data for the cleavage of Δ,Λ-$Cl(en)_2Cr(OH)Cr(en)_2Cl^{3+}$ in 9 and 12 M HClO₄, and in 9 and 12 M HCl are also reported.

It is well established that hydroxo-bridged oligomers of metal ions in concentrated solutions of strong acids are cleaved to give the "parent" monomeric species. Such reactions were first reported by Werner[1-5] and by Pfeiffer,[6,7] who showed that the dinuclear chromium(III) and cobalt(III) species $L_4M(OH)_2ML_4^{4+}$ [$L_4 = (NH_3)_4$ or $(en)_2$] in concentrated hydrochloric or hydrobromic acid are cleaved to form monomeric species. Both Werner and Pfeiffer assumed, correctly, that these reactions proceed with retention of configuration. The dihydroxo-bridged species are forced to adopt a cis configuration, and these experiments therefore provided substantial evidence that the configuration of the isolated isomers of the monomeric species is cis.

These cleavage reactions must clearly proceed in at least two steps, with a monohydroxo-bridged species as an intermediate. In perchloric acid, the intermediate has been shown to be $(H_2O)L_4M(OH)ML_4(H_2O)^{5+}$, and salts of this cation (or its deprotonated forms) have been isolated and characterized for M = Cr(III), Rh(III) and Ir(III) [$L_4 = (NH_3)_4$ or $(en)_2$].[9,10] The cleavage reactions of corresponding dihydroxo-bridged cobalt(III) species have been studied several times but the postulated monohydroxo-bridged intermediates have never been characterized.[11]

The corresponding cleavage reactions in HCl (or HBr) have not been studied in detail, nor have the intermediates been characterized. Furthermore, the nature of the initial monomeric products is in doubt, since the reported products could in some cases have arisen by anation of the initial cleavage products. The reaction path for these cleavage reactions has therefore been unknown until now. However, in this context it should be mentioned that it has been suggested on the basis of kinetic data that cleavage of Δ,Λ-$(en)_2Co(OH)_2Co(en)_2^{4+}$ in 1 M HCl proceeds via a monohydroxo-bridged species containing coordinated chloride.[12]

As a continuation of our studies[13-15] of the reactions of Δ,Λ-$(en)_2Cr(OH)_2Cr(en)_2^{4+}$ with various oxoanions in acidic solutions, a study of the chromium(III) species with hydrochloric acid was initiated. At moderate acid concentration ($C_{HCl} \sim 0.5$ M), this reaction affords the monohydroxo-bridged intermediate Δ,Λ-$Cl(en)_2Cr(OH)$ $Cr(en)_2Cl^{3+}$, which was isolated as a crystalline salt as described in this paper.

This new dinuclear species is one of the three possible singly-bridged intermediates which may be formed when Δ,Λ-$(en)_2Cr(OH)_2Cr(en)_2^{4+}$ is cleaved in 12 M HCl to monomeric species. A study of this reaction, as well as the cleavage of Δ,Λ-$Cl(en)_2Cr(OH)Cr(en)_2Cl^{3+}$ in 12 M HCl, has therefore been made and is presented in the following. The present work appears to be the first example of a detailed study of this type of cleavage reaction.

Experimental

Materials and instruments. The complexes Δ,Λ-[(en)$_2$Cr(OH)$_2$Cr(en)$_2$](ClO$_4$)$_4$ and Δ,Λ-[(HO)(en)$_2$Cr(OH)Cr(en)$_2$(OH)](ClO$_4$)$_3$ · 2H$_2$O were prepared as described in the literature.[8,16] All other chemicals were of analytical grade. Absorption spectra were recorded on a Perkin-Elmer Lambda Diode Array spectrophotometer using a resolution of 1.5 nm and a scan-time of 0.1 s per spectrum.

Analysis. C, H, N and Cl analyses were performed by the Microanalytical Laboratory at the H. C. Ørsted Institute, University of Copenhagen.

Preparation. Δ, Λ - μ - hydroxo - bis [chlorobis (ethylenediamine)-chromium(III)] diperchlorate chloride dihydrate, Δ,Λ-[Cl(en)$_2$Cr(OH)Cr(en)$_2$Cl](ClO$_4$)$_2$Cl · 2H$_2$O. A suspension of Δ,Λ-[(en)$_2$Cr(OH)$_2$Cr(en)$_2$](ClO$_4$)$_4$ (1 g, 1.29 mmol) in a mixture of 2.5 ml of 1 M HCl and 2.5 ml of 1 M LiCl was stirred at room temperature for 6 h. The starting materials dissolved within the first 3 h with separation of crystals of the dichloro complex. The mixture was then kept overnight at ~ 3 °C. The product was filtered off and washed carefully with 96 % ethanol. Yield 0.66 g (73 %).

The visible absorption spectrum of the product did not change after recrystallization, which was carried out as follows: The product (0.5 g) was dissolved in ice-cold water (30 ml) and saturated solutions of NaClO$_4$ (7 ml) and 6 M LiCl (1 ml) were then added to the filtered solution, which was cooled in ice. In order to minimize hydrolysis of the chloro complex this procedure was performed as fast as possible (≈ 2 min). Crystals of the dichloro dimer separated within minutes and were isolated as described above. Yield 0.32 g (64 %). Spectral data in 1 M NaClO$_4$ (extrapolated to t_0) (ε in l·mol^{-1} cm^{-1}, λ in nm): $(\varepsilon,\lambda)_{max}$ = (159,527); (132,389). $(\varepsilon,\lambda)_{min}$ = (44,446). The same values were obtained for solutions in 1 M HCl, 6 M HCl and 9 M HCl. Found: C, 13.68; N, 15.93; Cl, 24.10; H, 5.42. Calc. for Cr$_2$C$_8$H$_{37}$N$_8$O$_{11}$Cl$_5$: C, 13.66; N, 15.95; Cl, 25.22; H, 5.31. In addition to these analyses, total Cl$^-$ was determined by addition of excess AgNO$_3$ and potentiometric titration of the excess Ag$^+$ with Cl$^-$. The content of uncoordinated chloride was determined by potentiometric titration with AgNO$_3$ at 0 °C as fast as possible (~ 2 min): Total Cl$^-$: Found: 14.59. Calc.: 15.14. Uncoordinated Cl$^-$: Found: 4.92. Calc.: 5.05.

In aqueous neutral or slightly acidic solution, the dichloro dimer hydrolyzes to form the parent mono- and dihydroxo-bridged species, as shown spectrophotometrically. The spectrum of an aqueous solution changed with time and became almost constant within 120 min at 25 °C. The half-life was about 20 min. The final $(\varepsilon,\lambda)_{max}$ values were (175,529) and (111,383), which are nearly identical to the $(\varepsilon,\lambda)_{max}$ values (178,528) and (115,384) reported[8,16] for an equilibrium mixture of Δ,Λ-(en)$_2$Cr(OH)$_2$Cr(en)$_2^{4+}$ and Δ,Λ-(H$_2$O)(en)$_2$Cr(OH)Cr(en)$_2$(OH)$^{4+}$.

In basic solution the dichloro dimer forms the corresponding dihydroxo dimer, Δ,Λ-(HO)(en)$_2$Cr(OH)Cr(en)$_2$(OH)$^{3+}$, as shown spectrophotometrically. The spectral data for the dichloro dimer are similar to those for the dihydroxo dimer [$(\varepsilon,\lambda)_{max}$ = (159,526)], but significantly different from those for the diaqua dimer, Δ,Λ-(H$_2$O)(en)$_2$Cr(OH)Cr(en)$_2$(H$_2$O)$^{5+}$ [$(\varepsilon,\lambda)_{max}$ = (161,503)].[8] The identity of the product was therefore established as follows: A 5×10^{-3} M solution of Δ,Λ-[Cl(en)$_2$Cr(OH)Cr(en)$_2$Cl](ClO$_4$)$_2$Cl · 2H$_2$O in 0.05 M NaOH was kept at room temperature for 15 min and then cooled in ice. An equal volume of ice-cold 1 M HClO$_4$ was then added, and the spectrum was recorded as quickly as possible. The spectrum [$(\varepsilon,\lambda)_{max}$ = (160,505)] was virtually identical to that of Δ,Λ-[(HO)(en)$_2$Cr(OH)Cr(en)$_2$(OH)](ClO$_4$)$_3$ · 2H$_2$O in 1 M HClO$_4$ [$(\varepsilon,\lambda)_{max}$ = (162,505.5)].[8] The half-life for the reaction in 0.05 M NaOH was estimated to be about 2 min at 25 °C.

Kinetic data. Pseudo first-order rate constants, k_{obs}, were calculated from the absorbance A as a function of time t by means of non-linear regression analysis using the expression

$$A = A_\infty + (A_0 - A_\infty) \exp(-k_{obs}t).$$

These calculations were typically based upon absorbances measured at ~ 230 different wavelengths in the region 300–650 nm. The values of k_{obs} given in Table 1 are, in each case, the average of at least two determinations.

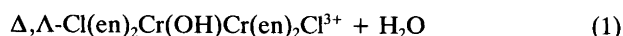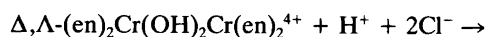*Table 1.* Experimental results for the cleavage reactions at 1.0 °C.

Reactant	Medium	k_{obs}/s^{-1}	Yields[a] of cis-Cr(en)$_2$(H$_2$O)$_{2-n}$Cl$_n^{(3-n)+}$ / %		
			$n = 0$	$n = 1$	$n = 2$
Δ,Λ-Cl(en)$_2$Cr(OH)Cr(en)$_2$Cl^{3+}	12 M HCl	>0.05		60.0	40.0
	9 M HCl	0.023(3)		63.4	36.6
	12 M HClO$_4$	>0.05		100[b]	
	9 M HClO$_4$	0.010(1)		100[b]	
Δ,Λ-(en)$_2$Cr(OH)$_2$Cr(en)$_2^{4+}$	12 M HCl	0.012(1)[c]	43.4	18.5	38.1

[a]The yields have been normalized so that the sum equals 100 % for each reaction. The accuracy is estimated to be ±1 % for each of the values. [b]See discussion in the text. [c]This value refers to the cleavage of the second bridge. For cleavage of the first bridge it is found that $k_2 > 0.1$ s^{-1}.

Product analysis for the cleavage reactions. The products formed in the cleavage reactions of Δ,Λ-[Cl(en)$_2$Cr(OH)Cr (en)$_2$Cl](ClO$_4$)$_2$ · 2H$_2$O and Δ,Λ-[(en)$_2$Cr(OH)$_2$Cr(en)$_2$] (ClO$_4$)$_4$ in hydrochloric acid and perchloric acid were analyzed by cation-exchange chromatography. The product solutions were diluted 40 times with ice-cold water and then adsorbed on a pre-cooled column of Dowex 50W-X2 cation exchanger within 5–6 min. The column was washed with large amounts of water. Elution with HNO$_3$ gave two or three well-separated bands. The first two bands were eluted with 2 M HNO$_3$, and the third band was then eluted with 4 M HNO$_3$. Each fraction was analyzed for chromium(III) by oxidation to CrO$_4^{2-}$ with H$_2$O$_2$ in basic solution. The content of CrO$_4^{2-}$ was determined spectrophotometrically (ε = 4826 M^{-1} cm^{-1} at 373 nm). In some experiments the content of coordinated chloride in each fraction was also determined by potentiometric titration with Ag$^+$. These determinations confirmed that the fractions contain, in order of elution: cis-Cr(en)$_2$Cl$_2^+$ (purple band), cis-Cr(en)$_2$ (H$_2$O)Cl^{2+} (reddish-purple band) and cis-Cr(en)$_2$(H$_2$O)$_2^{3+}$ (orange band). The recovery of chromium(III) was 96– 98 %. The yields given in Table 1 are relative to the amount of chromium(III) recovered and are the average of at least two determinations.

Results

Synthesis of Δ, Λ - [Cl (en)$_2$ Cr (OH) Cr (en)$_2$ Cl] (ClO$_4$)$_2$ Cl · 2H$_2$O. The binuclear cation Δ,Λ-(en)$_2$Cr(OH)$_2$ Cr(en)$_2^{4+}$ reacts in 0.5 M HCl, 0.5 M LiCl, as shown in eqn. (1), and the monohydroxo-bridged dichloro complex was isolated as a mixed chloride perchlorate salt (yield 73 %).

$$\Delta,\Lambda\text{-(en)}_2\text{Cr(OH)}_2\text{Cr(en)}_2^{4+} + \text{H}^+ + 2\text{Cl}^- \rightarrow$$

$$\Delta,\Lambda\text{-Cl(en)}_2\text{Cr(OH)Cr(en)}_2\text{Cl}^{3+} + \text{H}_2\text{O} \qquad (1)$$

Spectrophotometric monitoring of the reaction in 1 M HCl showed at least two reaction phases. The reaction has an overall half-life of about 10 min at 25 °C. By comparing the final spectrum with that of the dichloro dimer, it is estimated that the reaction in 1 M HCl affords the dichloro dimer in a yield of ≤ 50 %. The remaining species are probably also dinuclear species, since cleavage to monomeric species under these conditions can be ignored. It therefore seems likely that the product solution is an equilibrium mixture which, in addition to the isolated dichloro dimer, contains other monohydroxo-bridged species such as Cl(en)$_2$Cr(OH)Cr(en)$_2$(H$_2$O)$^{4+}$ and (H$_2$O)(en)$_2$Cr(OH) Cr(en)$_2$(H$_2$O)$^{5+}$.

The proposed structure of the new complex follows from several independent observations: Analytical data for the salt were in agreement with the formula Δ,Λ-[Cl(en)$_2$Cr (OH)Cr(en)$_2$Cl](ClO$_4$)$_2$Cl · 2H$_2$O; furthermore, the ratio Cl$^-$ (uncoordinated): Cl$^-$ (total): Cl (total) was found to be 1.01:3.00:4.96, in agreement with the calculated ratio of 1:3:5. The monohydroxo-bridged structure with two termi-

nal chloride ligands both coordinated in *cis* position with respect to the hydroxo bridge is in keeping with the well-known tendency of chromium(III) to undergo thermal substitution processes without rearrangement.

The position of the first ligand field band (λ_{max} = 527 nm) is 870 cm^{-1} red-shifted relative to that for Δ,Λ-(H$_2$O)(en)$_2$ Cr(OH)Cr(en)$_2$(H$_2$O)$^{5+}$ [λ_{max} = 503 nm in 1 M HClO$_4^8$ and 504 nm in 12 M HCl (measured in this study)]. In agreement with the average environment rule, this difference is about half that observed (1700 cm^{-1}) for the mononuclear species cis-Cr(en)$_2$Cl$_2^+$ (λ_{max} = 530 nm)^{21} and cis-Cr(en)$_2$ (H$_2$O)$_2^{3+}$ (λ_{max} = 486 nm),^{16} thus providing strong evidence that the complex contains one coordinated chloride per chromium(III). Further strong evidence for the proposed structure was obtained by the hydrolysis and cleavage experiments presented below and in the following section. Finally, the proposed structure has also been confirmed by a preliminary crystal structure analysis of Δ,Λ-[Cl(en)$_2$Cr (OH)Cr(en)$_2$Cl](ClO$_4$)$_2$Cl · 2H$_2$O.^{17}

The dichloro dimer hydrolyzes fairly rapidly in aqueous solution. In neutral or slightly acidic solution it hydrolyzes slowly ($t_\frac{1}{2} \sim$ 20 min at 25 °C), giving an equilibrium mixture of Δ,Λ-(H$_2$O)(en)$_2$Cr(OH)Cr(en)$_2$(OH)$^{4+}$ and Δ,Λ-(en)$_2$ Cr(OH)$_2$Cr(en)$_2^{4+}$, as shown spectrophotometrically. In 0.05 M NaOH it hydrolyzes ($t_\frac{1}{2} \sim$ 2 min at 25 °C) to Δ,Λ-(HO)(en)$_2$Cr(OH)Cr(en)$_2$(OH)$^{3+}$, as shown spectrophotometrically.

The cleavage in strong acids. General remarks. The reactions of Δ,Λ-[Cl(en)$_2$Cr(OH)Cr(en)$_2$Cl]Cl(ClO$_4$)$_2$ · 2H$_2$O and Δ,Λ-[(en)$_2$Cr(OH)$_2$Cr(en)$_2$](ClO$_4$)$_4$ in concentrated HCl and in concentrated HClO$_4$ yield mixtures of cis-Cr(en)$_2$(H$_2$O)$_2^{3+}$, cis-Cr(en)$_2$(H$_2$O)Cl^{2+} and cis-Cr(en)$_2$Cl$_2^+$. The reactions were studied spectrophotometrically and the product distributions were determined using cation-exchange chromatography.

Cleavage of Δ,Λ-Cl(en)$_2$Cr(OH)Cr(en)$_2$Cl^{3+}. Kinetic data for the cleavage of the dichloro dimer in 9 M and 12 M HCl, and in 9 M and 12 M HClO$_4$ at 1.0 °C were obtained from spectrophotometric measurements in the region 300– 600 nm. The reactions in 9 M HCl and in 9 M HClO$_4$ followed first-order kinetics for at least $6 \times t_\frac{1}{2}$, giving the rate constants listed in Table 1. The reactions in 12 M HCl and in 12 M HClO$_4$ are fast compared to the time required to dissolve the complex salt, and only an estimate of the lower limits for the rate constants could be obtained (Table 1).

Analysis of the product solutions by cation chromatography gave the results shown in Table 1. Cleavage of the dichloro dimer in HCl yields a mixture of cis-Cr(en)$_2$ (H$_2$O)Cl^{2+} and cis-Cr(en)$_2$Cl$_2^+$. The cleavage of the dichloro dimer is several orders of magnitude faster than the hydrolysis and anation reactions of the monomeric species. The pseudo first-order rate constant for the equilibration reaction between cis-Cr(en)$_2$(H$_2$O)$_2^{3+}$ and cis-Cr(en)$_2$(H$_2$O) Cl^{2+} in 12 M HCl is $\sim 5 \times 10^{-5}$ s^{-1} at 1.0 °C; for the equilibration between cis-Cr(en)$_2$Cl(H$_2$O)$^{2+}$ and cis-Cr(en)$_2$Cl$_2^+$
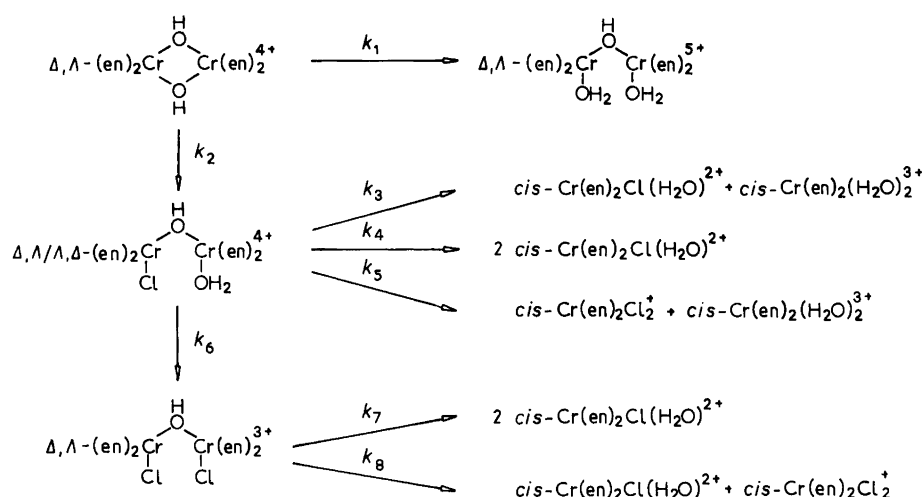
Scheme 1. The possible pathways for the cleavage in hydrochloric acid and in perchloric acid.

the value is $\sim 3 \times 10^{-5}$ s^{-1}.[18] These reactions therefore do not contribute to the product distribution. This was further confirmed for each of these reactions by showing that the product distribution was identical (within experimental error) for different reaction times, e.g. $6 \times t_{\frac{1}{2}}$ (cleavage) and $9 \times t_{\frac{1}{2}}$ (cleavage).

The major product of the cleavage in HClO$_4$ is cis-Cr(en)$_2$(H$_2$O)Cl^{2+}. cis-Cr(en)$_2$(H$_2$O)$_2^{3+}$ could not be detected, but a small amount (2 %) of cis-Cr(en)$_2$Cl$_2^+$ was found for the reaction of a 3×10^{-3} M solution of the dichloro dimer in 9 M HClO$_4$. The formation of cis-Cr(en)$_2$Cl$_2^+$ is attributed to the presence of chloride arising from the anions of the complex salt. This explains the fact that the yield of cis-Cr(en)$_2$Cl$_2^+$ was found to increase when the complex concentration was increased: for 3×10^{-3}, 9×10^{-3} and 9×10^{-2} M complex in 9 M HClO$_4$, the yields of cis-Cr(en)$_2$Cl$_2^+$ were 2 %, 7 % and 18 %, respectively. The visible absorption spectra of the product solutions (3×10^{-3} M complex) were identical for the two acid concentrations (9 and 12 M HClO$_4$) and the observed values [$(\varepsilon,\lambda)_{max}$ = (70,511.5) and (56,387)] are nearly identical to those reported for cis-Cr(en)$_2$Cl(H$_2$O)$^{2+}$.[19–21] It is therefore concluded that the reactions of Δ,Λ-[Cl(en)$_2$Cr(OH)Cr(en)$_2$

Cl](ClO$_4$)$_2$Cl · 2H$_2$O at low complex concentrations yields cis-Cr(en)$_2$(H$_2$O)Cl^{2+} quantitatively.

The data for the cleavage in HCl may be interpreted in terms of an aquation path and an anation path (Scheme 1). The pseudo first-order rate constants for these pathways, k_7 and k_8, are given in Table 2 and have been calculated from the observed rate constants and the product distributions listed in Table 1. The cleavage in 9 and 12 M HClO$_4$ proceeds entirely by an aquation path, so that k_{obs} for these solutions corresponds to k_7 in Scheme 1.
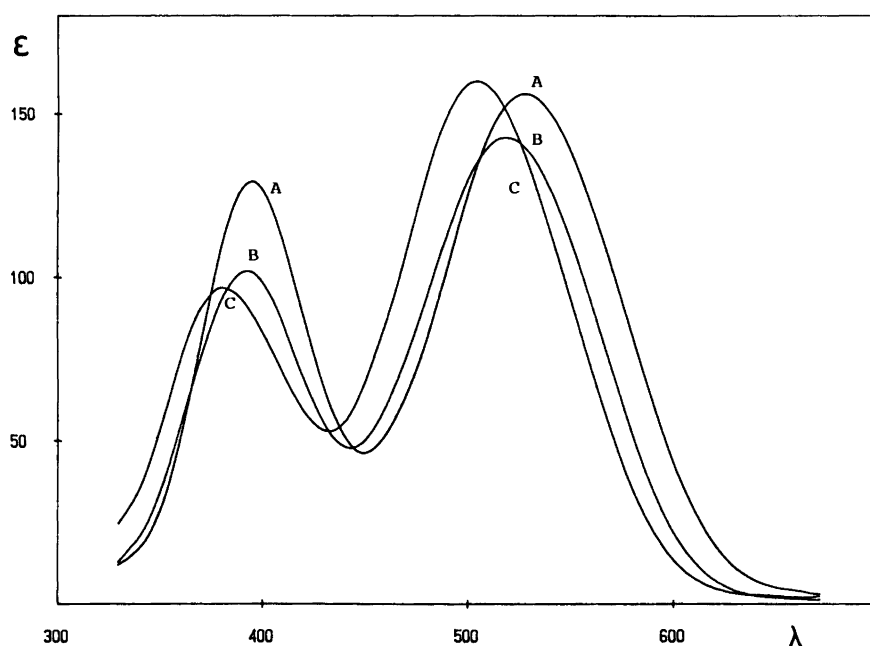
Cleavage of Δ,Λ-(en)$_2$Cr(OH)$_2$Cr(en)$_4^{4+}$. The cleavage of Δ,Λ-[(en)$_2$Cr(OH)$_2$Cr(en)$_2$](ClO$_4$)$_4$ in 12 M HCl at 1.0 °C was studied spectrophotometrically. The first spectrum was recorded 20 s after the time of dissolution, and the subsequent change of the absorbance with time followed first-order kinetics for at least $6 \times t_{\frac{1}{2}}$ and gave k_{obs} = 0.012 s^{-1}. The spectrum extrapolated back to the time of dissolution [$(\varepsilon,\lambda)_{max}$ = (143,517); (102,392)] is significantly different from that of the dihydroxo-bridged species (λ_{max} = 539.5). It is therefore concluded that the reaction, as anticipated, proceeds in two steps: a fast step with $k > 0.1$ s^{-1} and a slow step with k = 0.012 s^{-1}.

Table 2. Kinetic data for cleavage reactions in HCl and HClO$_4$ at 1.0 °C.

Reactant	Medium	Cleavage with aquation / %	Cleavage with anation / %	Pseudo first-order rate constants / s^{-1}
Δ,Λ-Cl(en)$_2$Cr(OH)Cr(en)$_2$Cl^{3+}	12 M HClO$_4$	100		$k_7 > 0.05$
	9 M HClO$_4$	100		k_7 = 0.010(1)
	12 M HCl	20(2)	80(2)	$k_7 > 0.01$; $k_8 > 0.04$
	9 M HCl	27(2)	73(2)	k_7 = 0.006(1); k_8 = 0.017(2)
Δ,Λ-(en)$_2$Cr(OH)$_2$Cr(en)$_2^{4+}$	12 M HCl	<5	>95	$k_2 > 0.1$; $k_1 \ll k_2$.[a]
$\Delta,\Lambda/\Lambda,\Delta$-Cl(en)$_2$Cr(OH)Cr(en)$_2$(H$_2$O)$^{4+}$	12 M HCl	18(7)	82(7)	k_{obs} = 1.2$\times 10^{-2}$ s^{-1}.[b]

[a] In the subsequent calculations (Table 3) the aquation path (k_1) has been ignored. [b] See also Table 3.

The most probable products for the first step are the diaqua dimer, Δ,Λ-(H$_2$O)(en)$_2$Cr(OH)Cr(en)$_2$(H$_2$O)$^{5+}$, and the aquachloro dimer, $\Delta,\Lambda/\Lambda,\Delta$-Cl(en)$_2$Cr(OH)Cr (en)$_2$(H$_2$O)$^{4+}$. The fact that the cleavage of the dihydroxo-bridged complex to mononuclear species ($t_{\frac{1}{2}} = 58$ s) is 15 times faster than the cleavage of Δ,Λ-(H$_2$O)(en)$_2$Cr(OH) Cr(en)$_2$(H$_2$O)$^{5+}$ ($t_{\frac{1}{2}} = 855$ s in 12 M HCl at 1 °C)[18] shows that a reaction path involving the latter ion does not contribute significantly to the cleavage of Δ,Λ-(en)$_2$Cr(OH)$_2$ Cr(en)$_2$$^{4+}$. It is therefore assumed that the cleavage occurs via the aquachloro dimer, $\Delta,\Lambda/\Lambda,\Delta$-Cl(en)$_2$Cr(OH)Cr(en)$_2$ (H$_2$O)$^{4+}$. The visible absorption spectrum of the intermediate supports this proposal. This spectrum is shown in Fig. 1 together with the spectra of the parent diaqua and dichloro dimers. The positions of the first ligand field bands for the diaqua and dichloro dimers are 504 nm and 527 nm, respectively. Using the average environment rule, it is predicted that the first ligand field band for the aquachloro dimer should be positioned at 515 nm, which is close to the value found for the intermediate (517 nm). It is therefore

concluded that the first and fast step of the hydrolysis of Δ,Λ-(en)$_2$Cr(OH)$_2$Cr(en)$_2$$^{4+}$ in 12 M HCl yields quantitatively (> 95 %) $\Delta,\Lambda/\Lambda,\Delta$-Cl(en)$_2$Cr(OH)Cr(en)$_2$(H$_2$O)$^{4+}$.

Analysis of the final product mixture by cation chromatography showed the presence of all three monomeric species, cis-Cr(en)$_2$(H$_2$O)$_2$$^{3+}$, cis-Cr(en)$_2$(H$_2$O)Cl^{2+} and cis-Cr (en)$_2$Cl$_2^+$ (Table 1). At 1.0 °C, the cleavage of the dihydroxo-bridged species in 12 M HCl ($t_{\frac{1}{2}} \approx 58$ s) is 300–400 times faster than the equilibration reactions[18] of the monomeric species. The latter reactions, therefore, do not contribute significantly to the product distribution. This was further confirmed by the observation that identical product distributions were obtained for reaction times equal to $6 \times t_{\frac{1}{2}}$ and $8 \times t_{\frac{1}{2}}$.

The aquachloro dimer may be cleaved by the three reaction paths corresponding to k_3, k_4 and k_5 (Scheme 1). In addition to these direct cleavage reactions, the cleavage may proceed via the dichloro dimer. For this pathway, the rate-determining step must be the reaction of the aquachloro dimer with chloride (k_6); the subsequent cleavage of

Table 3. Pseudo first-order rate constants for the cleavage of $\Delta,\Lambda/\Lambda,\Delta$-Cl(en)$_2$Cr(OH)Cr(en)$_2$(H$_2$O)$^{4+}$ in 12 M HCl at 1.0 °C (see Scheme 1).[a]

Comment	$k_3/$s^{-1}	$k_4/$s^{-1}	$k_5/$s^{-1}	$k_6/$s^{-1}
No cleavage via dichloro dimer	1.3(4) × 10^{-3} [11(3) %]	1.6(3) × 10^{-3} [13(2) %]	9.1(8) × 10^{-3} [76(2) %]	0 [0 %]
Maximum (13 %) cleavage via dichloro dimer	2.5(4) × 10^{-3} [21(3) %]	0 [0 %]	7.9(7) × 10^{-3} [66(2) %]	1.6(3) × 10^{-3} [13(2) %]
Average	2(1) × 10^{-3}	1(1) × 10^{-3}	8.5(14) × 10^{-3}	1(1) × 10^{-3}

[a]The numbers in square brackets are the contributions made by the individual reactions.

the dichloro dimer is fast ($t_{\frac{1}{2}} < 14$ s) and yields 60 % cis-$Cr(en)_2(H_2O)Cl^{2+}$ and 40 % cis-$Cr(en)_2Cl_2^+$, as described above. From this product distribution and from the observed product distribution for the present reaction it is possible to calculate the lower and upper limits to the contribution of each of the four reactions, and thereby also the limiting values for the four rate constants k_3, k_4, k_5 and k_6 shown in Table 3.

Discussion

The cleavage of Δ,Λ-$(en)_2Cr(OH)_2Cr(en)_2^{4+}$ occurs via a monohydroxo-bridged intermediate. In both 1 M HCl and 12 M HCl, the cleavage of the first bridge is much faster than the cleavage of the second. A similar difference in reactivity of the two bridges has been reported for the cleavage in perchloric acid.[8] In the present study, the different reactivities of the mono- and dihydroxo-bridged species have made it possible to characterize the aquachloro dimer, $\Delta,\Lambda/\Lambda,\Delta$-$Cl(en)_2Cr(OH)Cr(en)_2(H_2O)^{4+}$, in solution and to isolate stable crystalline salts of the dichloro dimer, Λ,Δ-$Cl(en)_2Cr(OH)Cr(en)_2Cl^{3+}$.

The cleavage of several singly- and doubly-bridged chromium(III) species has been studied previously, and for [H$^+$] in the region 10^{-6} to 1.0 M it is found that spontaneous hydroxo bridge cleavage dominates: For $(NH_3)_4Cr(OH)_2Cr(NH_3)_4^{4+}$, the acid-catalyzed path contributes by only 30 % for the first bridge cleavage in 1 M HClO$_4$.[22] For the cleavage of the first bridge of the racemic or meso isomers of $(en)_2Cr(OH)_2Cr(en)_2^{4+}$, the contribution of the acid-catalyzed path is negligible for 1 M HClO$_4$.[8,23] For the cleavage of $(NH_3)_5Cr(OH)Cr(NH_3)_5^{5+}$ and the so-called erythro analogues to monomeric species, the acid-catalyzed path could not be detected for [H$^+$] $\leq$ 1 M.[24,25]

The cleavage reactions studied in this work have been conducted at very high acid concentrations (9–12 M). Under these conditions the cleavage is orders of magnitude faster than the cleavage in dilute acid. We therefore assume that the cleavage reactions studied in this work proceed essentially via an acid-catalyzed pathway.

The first bridge cleavage of Δ,Λ-$(en)_2Cr(OH)_2Cr(en)_2^{4+}$ in 12 M HCl yields $\Delta,\Lambda/\Lambda,\Delta$-$(H_2O)(en)_2Cr(OH)Cr(en)_2Cl^{4+}$ quantitatively, i.e. the contribution from a reaction path which involves formation of the intermediate Δ,Λ-$(H_2O)(en)_2Cr(OH)Cr(en)_2(H_2O)^{5+}$ is negligible ($<5\%$). The subsequent reactions of Δ,Λ-$(H_2O)(en)_2Cr(OH)Cr(en)_2Cl^{4+}$ involve direct cleavage and cleavage via Δ,Λ-$Cl(en)_2Cr(OH)Cr(en)_2Cl^{3+}$.

The cleavage of the aquachloro and dichloro species in 9–12 M HCl proceeds by aquation and by anation pathways. For both species, the latter reaction plays a dominant role and contributes by ca. 80 % for each of the species. The product distribution is nearly the same for the cleavage of the dichloro dimer in 9 and 12 M HCl, the anation reaction being slightly more pronounced in 12 M HCl. This might indicate that ion-pairing between chloride ion and

dimer is complete in 12 M HCl, and that the (protonated) ion-pair is the reactive species.

The cleavage of the aquachloro dimer may occur either at the $Cl(en)_2Cr$-fragment or at the $(H_2O)(en)_2Cr$-fragment. The two reaction paths lead to the same products for aquation (k_3), but to different products for the anation (k_4 or k_5). The present data therefore distinguish the two pathways only in the latter case. It is seen that cleavage (by anation) at the $Cl(en)_2Cr$-fragment (k_5) is at least 6 times faster than cleavage at the $(H_2O)(en)_2Cr$-fragment (k_4). Similarly, it has been suggested that for cleavage of trans-$(NH_3)_5Cr(OH)Cr(NH_3)_4Cl^{4+}$ in hydrochloric acid there is a strong preference for cleavage at the $Cl(NH_3)_4Cr$-fragment, although quantitative data for this reaction have not been reported.[24]

The cleavage of the dichloro dimer in 12 M HCl is at least 5 times faster than the cleavage of the aquachloro dimer, and this difference is found for both the aquation and the anation pathways ($k_7 \gg k_3$, and $k_8 \gg k_4 + k_5$). In terms of a predominantly acid-catalyzed cleavage this is a reasonable result. The acid-catalyzed path is generally assumed to involve protonation of the hydroxo bridge to form a labile aqua-bridged species. The dichloro dimer has the lowest charge and should therefore be more susceptible to protonation.

The cleavage of the aquachloro dimer might also occur via the dichloro dimer (k_6); the upper limit for the contribution by this reaction path is 13 %, and this limiting value gives the upper limit for the rate constant for the anation reaction in 12 M HCl: $k_6 \leq 1.6\times10^{-3}$ s^{-1}. This value is 80 times greater than the pseudo first-order rate constant for the anation of cis-$Cr(en)_2(H_2O)Cl^{2+}$ in 12 M HCl: $k = 2\times10^{-5}$ s^{-1}.[18] An increased reactivity of the dinuclear species could to some extent be rationalized in terms of charge effects, but it is noted that the charge per metal centre is the same for the mono- and the dinuclear species. Another explanation could be that bridging hydroxide, like terminally coordinated hydroxide, has a labilizing effect upon the neighbouring ligands.

Cleavage of $(NH_3)_4Cr(OH)_2Cr(NH_3)_4^{4+}$ has been reported[26] to give cis-$Cr(NH_3)_4(H_2O)_2^{3+}$ and cis-$Cr(NH_3)_4Cl_2^+$, and our own preliminary experiments confirm this. This strongly indicates that the reaction occurs via the formation of an aquachloro dimer, which then undergoes cleavage at the $Cl(NH_3)_4Cr$-fragment with 100 % anation. It is seen that this pathway corresponds to the dominant pathway for the cleavage of the ethylenediamine complex studied in this work. In view of the otherwise great similarity[8,22] between the ammine and ethylenediamine systems this seems to be a reasonable result, and it seems very probable that in the ammine system, the formation of the aquachloro dimer is also concomitant with cleavage of the first bridge. The cleavage products obtained for the analogous reactions of ammine and ethylenediamine systems of cobalt(III) indicate that these species are also cleaved by the reaction sequences presented in this study.[1-5]

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