Binuclear Complexes of Chromium(III). I. Thermodynamics and Kinetics of the Equilibrium between μ-Hydroxo and Di-μ-hydroxo Binuclear Complexes of Chromium(III) with Ethylenediamine as a Ligand

JOHAN SPRINGBORG [a] and HANS TOFTLUND [b]

[a] Chemistry Department, The Royal Veterinary and Agricultural University, DK-1871 Copenhagen V., Denmark and [b] Department of Chemistry, University of Odense, DK-5000 Odense, Denmark

The binuclear ion $meso$-[(en)$_2$Cr(OH)$_2$Cr(en)$_2$]$^{4+}$ (diol) is shown in acid solution to give very fast an equilibrium mixture with the corresponding mono-hydroxo bridged ions [(H$_2$O)(en)$_2$Cr(OH)·Cr(en)$_2$(OH)]$^{4+}$ (aquahydroxo mono-ol) and [(H$_2$O)(en)$_2$Cr(OH)Cr(en)$_2$(H$_2$O)]$^{5+}$ (diaqua mono-ol). The aquahydroxo mono-ol as well as its basic form, [(OH)(en)$_2$Cr(OH)Cr(en)$_2$(OH)]$^{3+}$ (dihydroxo mono-ol) were isolated as their perchlorate salts. The equilibrium constant K_{eq} = [aquahydroxo mono-ol]/[diol] was determined at $\mu = 1.00$ M, to be 0.84 at 0.8 °C and 0.76 at 20 °C. The acid dissociation constants, K_{a1} and K_{a2}, of the diaqua mono-ol were determined spectrophotometrically (pK_{a1} = 0.67) and potentiometrically (pK_{a2} = 7.94), respectively, at $\mu = 1.00$ M, at 0.8 °C. The kinetics of the equilibrium reaction between diol and mono-ol was studied spectrophotometrically at 0.8 °C and $\mu = 1.00$ M in the [H$^+$] range $10^{-5} - 1.00$ M, the rate expression being $-$d[diol]/dt = d[mono-ol]/dt = k_1[diol] $- k_{-1}K_{a1}/(K_{a1} + $[H$^+$])[mono-ol], where $k_1 = 0.0221$ min^{-1} is the pseudo first-order rate constant for the reaction of diol to aquahydroxo mono-ol and $k_{-1} = 0.0254$ min^{-1} is the true first-order rate constant for the reverse reaction. From kinetic data at 0.8 °C and 20 °C, the activation parameters $E_a(k_1)$ = 19.6 kcal/mol and $E_a(k_{-1})$ = 20.7 kcal/mol were determined. The influence of ionic strength on K_{eq}, k_1 and k_{-1} was shown to be small.

In strongly basic solution, the diol deprotonates to give the blue μ-hydroxo-μ-oxo complex, which was isolated as its perchlorate salt, [(en)$_2$Cr(O)(OH)Cr(en)$_2$](ClO$_4$)$_3$.2H$_2$O.

Binuclear chromium(III) compounds with hydroxyl as a bridging ligand are known in cases with one, two or three hydroxo groups as

bridging ligands, $i.e.$ binuclear compounds belonging to the class of bridged structures called $mono$-ols, $diols$, and $triols$. So far most attention has been shown the mono-ols and the diols of chromium(III).

The classical mono-ols are the rhodo ion, [(NH$_3$)$_5$Cr(OH)Cr(NH$_3$)$_5$]$^{5+}$, and the erythro ion, [(NH$_3$)$_5$Cr(OH)Cr(NH$_3$)$_4$(H$_2$O)]$^{5+}$, which were both isolated by Jørgensen [1,2] in 1882. Later, a number of so-called acido erythro ions, [(NH$_3$)$_5$Cr(OH)Cr(NH$_3$)$_4$X]$^{4+}$ (X = Cl, Br, F, SCN, NO$_2$) have been reported.[3-6] The binuclear hydroxo-bridged structure of these compounds is now well established.[3-5,7-10]

Diols have been known since Pfeiffer [11] and Dubsky [12] nearly 70 years ago isolated salts of the ammonia diol, [(NH$_3$)$_4$Cr(OH)$_2$Cr(NH$_3$)$_4$]$^{4+}$, and of the ethylenediamine diol, [(en)$_2$Cr(OH)$_2$Cr(en)$_2$]$^{4+}$. The ethylenediamine diol, which is built up of two optically active units, is capable of existing in isomeric forms, $i.e.$ a $meso$ form and two optically active forms. It has recently been shown by an X-ray structure analysis on the salt [(en)$_2$Cr(OH)$_2$Cr(en)$_2$](ClO$_4$)$_2$Cl$_2$.2H$_2$O,[13] that the isomer isolated by Pfeiffer is the $meso$ form. Two other Cr(III) diols have had their structure determined by X-ray structure analysis, $meso$-[(gly)$_2$Cr(OH)$_2$Cr(gly)$_2$] and $racemic$-[(phen)$_2$Cr(OH)$_2$Cr(phen)$_2$]Cl$_4$.6H$_2$O.[14,15]

Both mono-ols and diols are known to undergo acid cleavage of the μ-hydroxo bridges giving the monomeric diaqua species. The acid cleav-

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age reaction of the rhodo ion and of several acido erythro ions has been studied kinetically and was found in perchlorate media to be independent of the hydrogen ion concentration.[5,6,16-18] Analogously, the acid cleavage reaction of the ethylenediamine diol has been shown in perchlorate media to be independent of the hydrogen ion concentration in the [H+] range 0.2 − 1.0 M,[19] whereas a first order dependence on [H+] has been reported for the rate of acid cleavage of the 1,10-phenanthroline diol in nitrate media.[20] Furthermore, the acid cleavage reactions of the aqua diol,[21] $[(H_2O)_4Cr(OH)_2Cr(H_2O)_4]^{4+}$, and the oxalato diol,[22] $[(ox)_2Cr(OH)_2Cr(ox)_2]^{4-}$, have been studied. The rate-laws showed a complex dependence on the hydrogen ion concentration.

To explain the kinetics of these cleavage reactions, a mono hydroxo bridged intermediate has been proposed. The intermediate is analogous to that proposed for interpreting the kinetics of the cleavage of analogous diols of Co(III).[23-26] In neither the Cr(III) nor the Co(III) systems has the mono-ol intermediate been isolated. Kinetic and thermodynamic data for the equilibrium between diol and mono-ol have been reported only for the equilibrium between the $[(H_2O)_5Cr(OH)Cr(H_2O)_5]^{5+}$ cation and the more well-characterized $[(H_2O)_4Cr(OH)_2Cr(H_2O)_4]^{4+}$ cation.[21]

In the present paper the equilibrium between meso-[(en)₂Cr(OH)₂Cr(en)₂]⁴⁺ and the corresponding mono-ols is studied.

A preliminary report has been published.[27]

EXPERIMENTAL

Materials. Sodium perchlorate and 70 % perchloric acid with the descriptions *"puriss. p.a."* were purchased from Fluka AG. Sodium hydroxide solutions were made from 'Titrisol' ampoules purchased from Merck. All other chemicals were analytical grade. For all spectrophotometric and potentiometric measurements carbon-dioxide-free, distilled water was used.

Instruments. A Zeiss DMR 21 spectrophotometer was used for all spectrophotometric measurements in the visible region. For the spectrophotometric data given below the absorbancy ε has been given in l mol⁻¹ cm⁻¹ and the wavelength λ has been given in nm. The molarity of solutions of the dimers was always defined as the number of mol of dimer and not the number of mol of chromium(III) per litre of solution. Infrared spectra of the compounds in potassium bromide discs were recorded on a Perkin-Elmer 457 grating infrared spectrophotometer.

The pH-measurements were made with a GK 2301 C combined glass and calomel electrode connected to a PHM 52 digital pH-meter, all from Radiometer, Copenhagen. The saturated potassium chloride calomel electrode was modified to 1 M sodium chloride in order to avoid precipitation of KClO₄ in the boundary between the medium and the electrode. The lower part of the electrode was placed in a flow-cell, which was cooled in an ice-bath. It was checked that the glass-electrode had an almost theoretical slope in the actual medium.

Analysis. Chromium analysis determined by atomic absorption spectrophotometry was performed by K. Jørgensen, Chemistry Department I, H. C. Ørsted Institute, and C, N, H, and Cl analyses were made by the microanalytical laboratory at the H. C. Ørsted Institute, Copenhagen.

Table 1. Spectral data in different media at 0 °C.

Sample	Medium	$(\varepsilon, \lambda)_{max}$	$(\varepsilon, \lambda)_{max}$
meso-[(en)₂Cr(OH)₂Cr(en)₂](ClO₄)₄	1 M NaClO₄	(199,539.5)	(107.386)
	1 M HClO₄	(199,539.5)	(107.385)
[(OH)(en)₂Cr(OH)Cr(en)₂(OH)](ClO₄)₃.2H₂O	1 M NaClO₄	(162,527.5)	(134,387)
	0.01 M NaOH, 1 M NaClO₄	(160,526.5)	(133,387)
[(H₂O)(en)₂Cr(OH)Cr(en)₂(OH)](ClO₄)₄	0.01 M NaOH, 1 M NaClO₄	(158,526.2)	(134,387)
	1.0 M NaOH	(159,525.2)	(135,384)
	1.0 M NaClO₄	(169,515.5)	(130,380.5)
	0.001 M HClO₄, 1 M NaClO₄	(169,515.5)	(129,380.5)
	0.005 M HClO₄, 1 M NaClO₄	(170,515.0)	(129,381.0)
	1 M HClO₄	(162,505.5)	(105,379)
[(H₂O)(en)₂Cr(OH)Cr(en)₂(H₂O)]⁵⁺	—	(161,503)ᵃ	(100,378)ᵃ

ᵃ Calculated, see text. The concentrations of complex were always ∼4×10⁻³ M.

Preparations. 1. meso-*Di-μ-hydroxobis[bis-(ethylenediamine)chromium(III)]* *perchlorate* and other salts of the diol. [(en)$_2$Cr(OH)$_2$-Cr(en)$_2$]X$_4$.nH$_2$O (X$_4$.nH$_2$O = Cl$_4$.2H$_2$O; (ClO$_4$)$_4$, and (ClO$_4$)$_2$Cl$_2$.2H$_2$O). The perchlorate and chloride salts were prepared and their purity checked as described in the literature.[28] Visible spectra of the perchlorate salt in different media are given in Table 1. The salt, *meso*-[(en)$_2$Cr(OH)$_2$-Cr(en)$_2$](ClO$_4$)$_2$Cl$_2$.2H$_2$O, which has been used for X-ray crystal-structure determination[13] was prepared in the following way. To a solution of *meso*-di-μ-hydroxobis[bis(ethylenediamine)chromium(III)]chloride dihydrate (0.4 g, 0.72 mmol) in water (10 ml) was added a mixture of 1.2 M hydrochloric acid (0.5 ml), a saturated solution of sodium perchlorate (1 ml), and ethanol (2 ml). The solution was slowly cooled to 0 °C, and after 1 h the blue-violet crystals were filtered off and washed with 96 % ethanol. (Found: Cr 15.08; C 14.01; N 16.64; H 5.53; Cl 20.80. Calc. for [(en)$_2$-Cr(OH)$_2$Cr(en)$_2$](ClO$_4$)$_2$Cl$_2$.2H$_2$O: Cr 15.20; C 14.04; N 16.38; H 5.60; Cl 20.72).

2. meso-*μ-Hydroxo-μ-oxo-bis[bis(ethylene-diamine)chromium(III)]* *perchlorate.* [(en)$_2$-Cr(O)(OH)Cr(en)$_2$](ClO$_4$)$_3$.2H$_2$O.*meso*-Di-μ-hydroxobis[bis(ethylenediamine)chromium-(III)] perchlorate (2.0 g, 2.6 mmol) was dissolved in 0 °C cold 2 M sodium hydroxide (80 ml). To the filtered solution was added, with stirring and cooling in ice, a saturated solution of sodium perchlorate (40 ml, room temperature). These operations were performed within 4 min in order to avoid hydrolysis. Green crystals of the perchlorate salt of the μ-hydroxo-μ-oxo complex precipitated almost instantaneously. The precipitate was filtered and washed with 96 % ethanol and dried in air. Yield 1.25 g (68 %). (Found: Cr 14.48; C 13.52; N 15.72; H 5.37; Cl 14.87. Calc. for [(en)$_2$Cr(O)-(OH)Cr(en)$_2$](ClO$_4$)$_3$.2H$_2$O: Cr 14.61; C 13.50; N 15.75; H 5.24; Cl 14.94). The solid salt, if kept dry, is stable for months at room temperature. In aqueous solution the colour changes rapidly and within minutes becomes reddish owing to the formation of the μ-hydroxo bridged cation, [(OH)(en)$_2$Cr(OH)Cr(en)$_2$(OH)]$^{3+}$. By addition of perchloric acid to freshly prepared solutions, the perchlorate salt of the *meso* diol re-formed instantaneously and nearly quantitatively. [(en)$_2$Cr(O)(OH)Cr(en)$_2$](ClO$_4$)$_3$.2H$_2$O (0.5 g, 0.70 mmol) was dissolved in water (10 ml) at 0 °C. To the blue solution was immediately added ice-cold 3 M perchloric acid (10 ml). The colour instantaneously turned violet and within seconds the perchlorate salt of *meso* diol precipitated. The precipitate was filtered off and washed with 96 % ethanol and ether. Drying in air yielded 0.47 g (yield 86 %) of pure *meso*-[(en)$_2$Cr(OH)$_2$Cr(en)$_2$](ClO$_4$)$_4$, identified by its infrared spectrum in the region 4000 to 250 cm^{-1}.

3. *μ-Hydroxobis[bis(ethylenediamine)hydroxochromium(III)]* *perchlorate* *dihydrate.* [(OH)-

(en)$_2$Cr(OH)Cr(en)$_2$(OH)]ClO$_4$)$_3$.2H$_2$O. *meso*-Di-μ-hydroxobis[bis(ethylenediamine)chromium(III)] perchlorate (7.76 g, 10 mmol) was added to 1 M sodium hydroxide (11 ml) at 33 – 35 °C. A green precipitate of μ-hydroxo-μ-oxobis[bis(ethylenediamine)chromium(III)] perchlorate and a blue solution of the μ-hydroxo-μ-oxo cation were formed instantaneously. The suspension was kept at 33 – 35 °C with stirring for 12 – 14 min. Within half a minute the colour of the solution shifted to red owing to the formation of the μ-hydroxobis[bis(ethylene-diamine)hydroxochromium(III)] ion and after 10 min all the μ-hydroxo-μ-oxo salt had dissolved. To the resulting red solution, from which precipitation of red crystals of μ-hydroxobis[bis(ethylenediamine)hydroxochromium(III)] perchlorate had commenced, was added a saturated solution of sodium perchlorate (5 ml) and the suspension was cooled in ice for half an hour. The precipitate was filtered and washed with 96 % ethanol (four 10 ml portions). Drying in air yielded 4.50 g (62 %). The crude product was dissolved in 0.01 M sodium hydroxide (26 ml) at room temperature and a saturated solution of sodium perchlorate (13 ml) was added to the filtered solution with stirring and cooling in ice. After 10 min the precipitate was filtered, washed with 96 % ethanol and dried in air. Yield 3.5 g (78 %). The sample reprecipitated twice was pure. (Found: Cr 14.23; C 13.32; N 15.55; H 5.52; Cl 14.70. Calc. for [(OH)(en)$_2$Cr(OH)·Cr(en)$_2$(OH)](ClO$_4$)$_3$.2H$_2$O: Cr 14.25; C 13.16; N 15.36; H 5.39; Cl 14.57). Visible spectral data in different media are given in Table 1. The solid salt is stable for months at room temperature. In aqueous solution the diol is re-formed nearly quantitatively as follows. [(OH)(en)$_2$Cr(OH)·Cr(en)$_2$(OH)](ClO$_4$)$_3$.2H$_2$O (0.729 g, 1.00 mmol) was dissolved at room temperature in 0.12 M perchloric acid (10 ml). The solution was kept at room temperature for 7 min and then a saturated solution of sodium perchlorate (10 ml) was added portionwise to the stirred solution during 3 min. After a further 10 min the precipitate was filtered off and washed with 96 % ethanol and ether. Drying in air yielded 0.72 g of pure *meso*-[(en)$_2$Cr(OH)$_2$Cr(en)$_2$](ClO$_4$)$_4$. Yield 93 %. The product was identified by its infrared spectrum in the region 4000 to 250 cm^{-1} and its visible absorption spectrum in 1 M NaClO$_4$ at 0 °C.

4. *Aquatetrakis(ethylenediamine)-μ-hydroxo-hydroxodichromium(III)* *perchlorate* [(H$_2$O)(en)$_2$-Cr(OH)Cr(en)$_2$(OH)](ClO$_4$)$_4$. μ-Hydroxobis-[bis(ethylenediamine)hydroxochromium(III)] perchlorate (2.00 g, 2.74 mmol) was cooled in ice. To the cold solid was then added ice-cold 0.6 M perchloric acid (6 ml). The mixture was vigorously shaken to obtain a solution which then immediately was filtered into an ice-cold mixture of water (3 ml) and a saturated (at room temperature) solution of sodium perchlorate (6 ml) with cooling in ice and stirring. These

operations were performed within 5 s. The precipitation of the aquahydroxo mono-ol salt instantaneously commenced. The solution was filtered after a further 30 s and immediately washed with 96 % ethanol (three 20 ml portions) and then with ether. The product was sucked dry in a vacuum-desiccator for 15 min, weighed and stored at -15 °C. Yield 1.6 g (73 %). (Found: Cr 13.00; C 12.21; N 14.16; H 4.60; Cl 17.70. Calc. for $[(H_2O)(en)_2Cr(OH)-Cr(en)_2(OH)](ClO_4)_4$: Cr 13.10; C 12.10; N 14.11; H 4.57; Cl 17.85). As a contamination of diol is likely and cannot be observed by the elementary analysis, a check of the purity was made spectrophotometrically. The spectrum was measured in 0.01 M NaOH, 1 M NaClO$_4$ (0 °C) and found to be identical to the spectrum of dihydroxo mono-ol (see Table 1).

At 60 °C the solid perchlorate salt gives diol very fast. Thus, heating of solid $[(H_2O)(en)_2-Cr(OH)Cr(en)_2(OH)](ClO_4)_4$ at 60 °C for 10 min yielded a violet product identified as nearly pure meso-$[(en)_2Cr(OH)_2Cr(en)_2](ClO_4)_4$ by comparing its visible absorption spectrum in 1 M NaClO$_4$ at 0 °C, $(\varepsilon, \lambda)_{max} = (198,539)$ and $(108,386)$, with that of authentic diol (see Table 1). The product showed an IR spectrum in the region $4000-250$ cm^{-1} very similar but not identical to that of authentic meso-$[(en)_2-Cr(OH)_2Cr(en)_2](ClO_4)_4$. At room temperature the perchlorate salt gives diol within a week, but at -15 °C it is stable for weeks. The perchlorate salt is very soluble in water. An aqueous solution gives nearly quantitatively the perchlorate salt of the diol as follows. $[(H_2O)(en)_2Cr(OH)-Cr(en)_2(OH)](ClO_4)_4$ (0.794 g, 1.00 mmol) was dissolved at room temperature in 0.012 M perchloric acid (10 ml). The solution was kept at room temperature for 7 min and then a saturated solution of sodium perchlorate (10 ml) was added portionwise to the stirred solution during 3 min. After a further 10 min the precipitate was filtered off and washed with 96 % ethanol and ether. Drying in air yielded 0.70 g of pure meso-$[(en)_2Cr(OH)_2Cr(en)_2](ClO_4)_4$. Yield 90 %. The product was identified by its infrared spectrum in the region 4000 to 250 cm^{-1} and by its visible absorption spectrum in 1 M NaClO$_4$ at 0 °C.

Potentiometric determination of the acid dissociation constant of the aquahydroxo mono-ol. Solutions of $[(OH)(en)_2Cr(OH)Cr(en)_2(OH)]-(ClO_4)_3 \cdot 2H_2O$ in 5×10^{-3} M HClO$_4$, 1.00 M NaClO$_4$ at 0 °C were prepared as described below for the spectrophotometric measurements and then immediately transferred to the flow-cell with suction. Reliable readings on the pH-meter could then be obtained about 1 min after the time of dissolution. The measurements were continued over a period of 5 min and the pH at the time of dissolution was then calculated by linear extrapolations. The definition pH = $-\log[H^+]$ was employed throughout, and concentration pH standards were made in the actual salt medium. Experimental results

are given in Table 2.

Spectra and kinetic runs. Nearly all spectrophotometric measurements were made in perchlorate medium with constant ionic strength at $\mu = 1.00$ M adjusted with NaClO$_4$. Owing to the rapid equilibrium between the diol and the mono-ols it was important that the interval between the time of dissolution of the complex (t_0) and the time for the first measurement on the spectrophotometer should be as short as possible. In solutions with $[ClO_4^-] = 1.00$ M, however, the perchlorate salts of the dimers dissolved slowly and this dictated the following method of preparation of the solutions. The solid dimer perchlorate was added to a known volume of water at the temperature of study. The mixture was then immediately vigorously shaken to give complete dissolution of the sample within 10 s of the addition of the complex. To the solution was then added the requisite amount of a solution of NaClO$_4$ (or HClO$_4$ + NaClO$_4$ etc.) by use of a thermostated syringe. The two media were mixed as fast as possible and the solution was rapidly transferred to the flow-cell with suction. A commercial 1 cm QS flow-cell (Helma) was used. Following the above procedure it was possible to make and transfer the solutions to the flow-cell within 25 s. The response of the spectrophotometer was a few seconds, which means that reliable measurements of the absorbancy could be obtained 30 s after the dissolution of the complex.

The temperature of the cell was kept constant by thermostating of the cell compartment of the Zeiss DMR 21 spectrophotometer. The temperature in the inner part of the cell was measured with a thermocouple. Nearly all measurements were performed at 0 °C. A small deviation between the temperature of the ice-bath and the equilibrium temperature (0.70 ± 0.05 °C) of the inner part of the cell was found. The temperature of the solutions, immediately

Table 2. Determination of the second acid dissociation constant of $[(H_2O)(en)_2Cr(OH)Cr(en)_2-(H_2O)]^{5+}$ in 1 M NaClO$_4$ at 0 °C. See text.

$10^3 \times C_{mono-ol}$ mol/l	pH	$\bar{n}$	pK_{a2}
3.254	2.768	1.008	
4.332	3.212	1.009	
4.691	3.605	1.010	
7.177	7.660	0.695	8.018
8.293	7.703	0.601	7.881
10.09	7.887	0.494	7.877
11.53	8.077	0.432	7.958
12.97	8.146	0.384	7.941
15.85	8.272	0.315	7.935
		pK_{a2}(av)	7.94

after they had been prepared and transferred to the cell ($t = 60$ s) was always slightly higher (0.9 °C) to decrease to the equilibrium temperature within 15 min. So, following strictly the same procedure for each measurement, the temperature could be reproduced throughout as 0.8 ± 0.1 °C.

The diol and the three mono-ols were all characterized by their absorption spectra in the region 650 – 340 nm at 0 °C and with $\mu = 1.00$ M adjusted with $NaClO_4$. The spectra of the perchlorate salts of the diol and of the aquahydroxo mono-ol in neutral or acid solution changed rapidly with time, and extrapolations back to the time of dissolution (t_0) were therefore required. These were performed either logarithmically or linearly. Logarithmical extrapolations were calculated using eqn. 1 given below. Linear extrapolations were based on curves taken 30 and 60 s, respectively, after t_0 and were never greater than 2 %. The spectra of the perchlorate salts of the aquahydroxo or dihydroxo mono-ols in basic solutions at 0 °C were constant for 10 min after t_0 and could, therefore, be measured without difficulty.

The kinetic measurements were performed by following the change of the absorbancy in the region 650 – 340 nm of solutions initially composed either of diol or mono-ol. The changes in absorbancy at the wavelengths 570, 560 and 550 nm, respectively, were used for the calculations of the rate constants, as in this region the greatest differences between the absorbancies of the diol and the diaqua or aquahydroxo mono-ols are found.

Treatment of kinetic data. With the exception of the measurements in pure 1 M $NaClO_4$, all kinetic measurements were made under pseudo first-order conditions, *i.e.* the change in the hydrogen ion concentration during a kinetic run was never greater than 2 %. Pseudo first-order rate constants for the equilibration reaction were determined by plotting log $(A_t - A_\infty)$ against time. Such plots were linear for more than 3 half-lives. The deviations observed after 3 $t_{\frac{1}{2}}$ were unsystematic and certainly due to an experimental error in the determination of the small differences $A_t - A_\infty$ in absorbancy. Rate

constants were calculated from the slope of the plots using the relationship

$$\ln(A - A\infty) = -k_{obs}t + \ln(A_0 - A\infty) \qquad (1)$$

The infinite time values, $A\infty$, were excellently defined for all kinetic runs in the acid solutions, *i.e.* absorption curves taken at $7t_{\frac{1}{2}}$ and $8t_{\frac{1}{2}}$, respectively, were identical within the experimental accuracy. For the kinetic runs in pure 1 M $NaClO_4$, constant absorption curves were never achieved, *i.e.* a very slow decrease of the absorbancy in the region 600 – 500 nm after $7t_{\frac{1}{2}}$ was observed. The readings of the absorbancy at $7t_{\frac{1}{2}}$ were then used as $A\infty$ values. Values of k_{obs} are given in Tables 3 and 4.
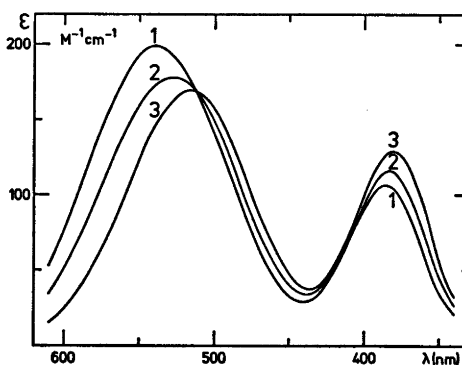

Fig. 1. Visible absorption spectra of *meso*-[(en)$_2$Cr(OH)$_2$Cr(en)$_2$](ClO$_4$)$_4$ (1) and [(H$_2$O)(en)$_2$Cr(OH)Cr(en)$_2$(OH)](ClO$_4$)$_4$ (3) in 10^{-3} M HClO$_4$, 1 M NaClO$_4$ at 0 °C extrapolated to the time of dissolution. The spectra of *meso*-[(en)$_2$Cr(OH)$_2$Cr(en)$_2$](ClO$_4$)$_4$ and [(H$_2$O)(en)$_2$Cr(OH)Cr(en)$_2$(OH)](ClO$_4$)$_4$, respectively, in 10^{-3} M HClO$_4$, 1 M NaClO$_4$ after 110 min were identical and nearly constant (2).

Table 3. Observed and calculated rate constants for the equilibrium between the diol and the mono-ols at 0.8 °C. See text. k_{calc} from eqn. (10).

C_{HClO_4} mol/l	$10^2 k_{obs}(D)$ min^{-1}	$10^2 k_{obs}(M)$ min^{-1}	$10^2 k_{obs}(av)$ min^{-1}	$10^2 k_{calc}$ min^{-1}
$\simeq 10^{-5}$	4.35	4.65	4.50	4.75
1.00×10^{-2}	4.65	4.73	4.69	4.74
4.00×10^{-2}	4.38	4.29	4.34	4.35
1.00×10^{-1}	3.83	3.97	3.90	3.95
3.00×10^{-1}	3.37	3.33	3.35	3.27
5.00×10^{-1}	3.03	3.11	3.07	2.98
1.00	2.81	2.48	2.65	2.66

Table 4. Kinetic and thermodynamic data in various media.

Medium	T °C	$10^2 k_{obs}(D)$ min^{-1}	$10^2 k_{obs}(M)$ min^{-1}	$10^2 k_{obs}(av)$ min^{-1}	$10^2 k_1$ min^{-1}	$10^2 k_{-1}$ min^{-1}	K_{eq}
10^{-3} M HClO$_4$, 1 M NaClO$_4$	20.0	52.9	55.7	54.3	23.5	30.8	0.763
$\mu = 1.00$ M	0.8	–	–	–	2.21[a]	2.54[a]	0.835[b]
10^{-3} M HClO$_4$	0.8	4.24	4.02	4.13	1.94	2.19	0.885

[a] Taken from Table 3 and Fig. 4. [b] Taken from Fig. 3.

RESULTS

Diol. The absorption spectra of aqueous solutions of salts of the diol, *meso*-[(en)$_2$Cr(OH)$_2$-Cr(en)$_2$]$^{4+}$, change rapidly with time owing to a fast equilibrium with the corresponding mono-ols, *i.e.* μ-hydroxo bridged, binuclear cations. In order to obtain the spectrum of the diol it was therefore necessary, even at 0 °C, to extrapolate these absorption curves to the time of dissolution (see Fig. 1). In Table 1 it is seen that the spectra in 1 M NaClO$_4$ and in 1 M HClO$_4$ at 0 °C are identical. Protonation of the diol to form a μ-aqua-μ-hydroxo complex in 1 M HClO$_4$ at 0 °C is, therefore, assumed not to occur to any considerable extent (probably less than 3 %). The lower limit to the acid dissociation constant, K_a, of the μ-aqua-μ-hydroxo complex is then estimated as $K_a \geq 30$ M. When the diol is dissolved in strongly basic solution, it gives a blue solution of its deprotonated form,

$$\left[(en)_2Cr \begin{matrix} H \\ O \\ \\ O \\ H \end{matrix} Cr(en)_2 \right]^{4+} + OH^- \rightleftharpoons$$

$$\left[(en)_2Cr \begin{matrix} H \\ O \\ \\ O \end{matrix} Cr(en)_2 \right]^{3+} + H_2O \qquad (2)$$
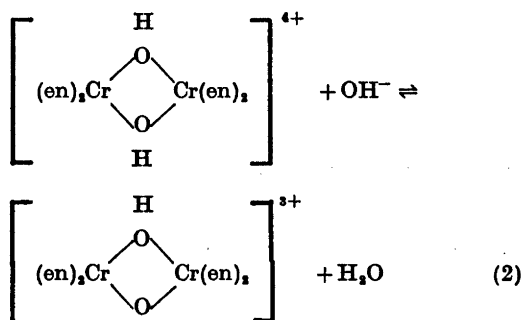
The μ-hydroxo-μ-oxo complex was isolated as a green perchlorate salt. From potentiometric and spectrophotometric measurements, the acid dissociation constant of the diol in pure water is roughly estimated as $pK_a \simeq 12$ at 20 °C.

Mono-ols. At room temperature, the colour of the basic solution of the blue μ-hydroxo-μ-oxo cation changes rapidly and within minutes becomes reddish owing to the formation of the μ-hydroxo bridged cation, [(OH)(en)$_2$Cr(OH)-Cr(en)$_2$(OH)]$^{3+}$, hereafter referred to as the dihydroxo mono-ol. This cation was isolated as a reddish brown perchlorate salt, [(OH)(en)$_2$-Cr(OH)Cr(en)$_2$ (OH)](ClO$_4$)$_3$.2H$_2$O, in high yield (62 %). One of the corresponding acid forms, the aquahydroxo mono-ol, was also isolated as a salt. So, when the perchlorate salt of the dihydroxo mono-ol was dissolved fast in perchloric acid and immediately added to a strong solution of sodium perchlorate, the aquahydroxo mono-ol precipitated as [(H$_2$O)(en)$_2$-Cr(OH)Cr(en)$_2$(OH)](ClO$_4$)$_4$ (yield 73 %). The isolation of the aquahydroxo mono-ol had to be performed fast, even at 0 °C, owing to the rapid formation of diol. The diaqua mono-ol, [(H$_2$O)(en)$_2$Cr(OH)Cr(en)$_2$(H$_2$O)]$^{5+}$, was not isolated as a salt, but characterized by its visible absorption spectrum and its acid dissociation constant as discussed later.

While the solid perchlorate salt of the dihydroxo mono-ol at room temperature is stable for months, the solid perchlorate salt of the aquahydroxo mono-ol gives almost quantitatively that of the diol within approximately a week at room temperature. At 60 °C solid aquahydroxo mono-ol gives diol within 10 min.

In aqueous solution these mono-ols can be transformed back to diol quantitatively. Thus, slightly acidified aqueous solutions of the mono-ols were left for 10 min at room temperature to ensure that equilibrium between mono-ol and diol had been established and NaClO$_4$ was then slowly added. By this the perchlorate salt of the diol, which is less soluble

than the perchlorate salt of the aquahydroxo mono-ol, precipitated quantitatively. For other anions, i.e. bromide, chloride, and dithionate, the salts of the diol are again the less soluble. This lower solubility of salts of the diol seems to be general.

The first and second acid dissociation constants, K_{a1} and K_{a2}, of the diaqua mono-ol were studied potentiometrically and spectrophotometrically. From the potentiometric measurements K_{a2} was determined as described below, whereas only a lower limit to K_{a1} could be estimated from these measurements. However, K_{a1} was then determined spectrophotometrically as shown in the following section.

The determination of pK_{a2} was performed by measuring pH in partly acidified solutions of [(OH)(en)$_2$Cr(OH)Cr(en)$_2$(OH)](ClO$_4$)$_3$.2H$_2$O. Because of the rapid conversion into diol a normal acidometric titration could not be performed. Therefore, solutions of [(OH)(en)$_2$-Cr(OH)Cr(en)$_2$(OH)](ClO$_4$)$_3$.2H$_2$O in 5×10^{-3} M HClO$_4$, 1 M NaClO$_4$ were made as rapidly as possible and the pH at the time of dissolution, pH$_0$, was then obtained by a linear extrapolation from the pH measurements within the first 5 min. For solutions with $\bar{n} < 1$, where $\bar{n}$ is defined as below, an increase of pH with time was observed and the rate of change was in the order of 0.01 pH unit per min. For solutions with $\bar{n} > 1$, pH was constant within the experimental accuracy.

K_{a2} was calculated by means of the equation:

$$pK_{a2} = -\log[H^+] + \log\left[\frac{\bar{n}}{1-\bar{n}}\right] - \log\left[1 + \frac{[H^+](2-\bar{n})}{K_{a1}(1-\bar{n})}\right] \quad (3)$$

where $\bar{n}$ equals the average number of protons taken up by the dihydroxo mono-ol and is given by

$$\bar{n} = (C_{HClO_4} - [H^+] + [OH^-])/C_{mono-ol} \quad (4)$$

where $C_{mono-ol}$ = stoichiometric concentration of the complex and C_{HClO_4} = stoichiometric concentration of perchloric acid added. The last term of eqn. 3 was ignored in the calculations of pK_{a2}. From the measurements with $0 < \bar{n} < 1$, the average value $pK_{a2} = 7.94$ was calculated as shown in Table 2.

A lower limit estimate of K_{a1} was obtained from the measurements with $\bar{n} > 1$. Using the equation

$$pK_{a1} = -\log\frac{[H^+]^2(2-\bar{n})}{K_{a2}\bar{n} + [H^+](\bar{n}-1)} \simeq$$
$$pH + \log\frac{(\bar{n}-1)}{(2-\bar{n})} \quad (5)$$

and an estimated accuracy (± 0.02 unit in pH) in the measured pH values, it is calculated that $pK_{a1} < 1.3$. This is in agreement with the spectrophotometrically determined value of $pK_{a1} = 0.67$.

The spectra (extrapolated to $t = t_0$) of [(H$_2$O)-(en)$_2$Cr(OH)Cr(en)$_2$(OH)](ClO$_4$)$_4$ in 1 M NaClO$_4$ and in slightly acid solutions at 0 °C were identical as shown in Table 1. These observations are in agreement with the low pK_{a1} of the diaqua mono-ol, and the spectra in these media therefore represent the spectrum of the aquahydroxo mono-ol cation (see also Fig. 1). In stronger acid solutions, a blue-shift of the first absorption band was observed, but even in 1 M HClO$_4$ (0 °C), the mono-ol is not fully protonated to diaqua mono-ol (see Table 1). The spectrum of the pure diaqua mono-ol shown in Fig. 2 (see also Table 1) was calculated from the spectra in 1 M HClO$_4$ and 10^{-3} M HClO$_4$, 1 M NaClO$_4$ (0 °C) by means of the spectrophotometrically determined value of $pK_{a1} = 0.67$.

The spectra of basic solutions (0.01 M NaOH, 1 M NaClO$_4$) of [(H$_2$O)(en)$_2$Cr(OH)Cr(en)$_2$(OH)]-
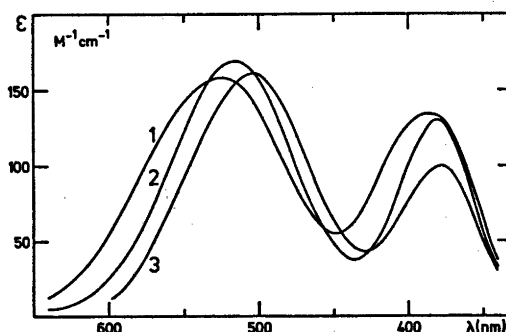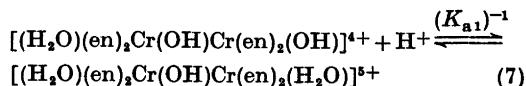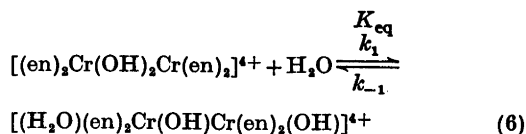

Fig. 2. Visible absorption spectra at 0 °C of 4×10^{-3} M solutions of [(H$_2$O)(en)$_2$Cr(OH)-Cr(en)$_2$(OH)](ClO$_4$)$_4$ in 0.01 M NaOH, 1 M NaClO$_4$ (1) and in 10^{-3} M HClO$_4$, 1 M NaClO$_4$ (2), and the calculated spectrum of [(H$_2$O)-(en)$_2$Cr(OH)Cr(en)$_2$(H$_2$O)]$^{5+}$ (3).

$(ClO_4)_4$ and $[(OH)(en)_2Cr(OH)Cr(en)_2(OH)]$-$(ClO_4)_3.2H_2O$ are identical and represent pure dihydroxo mono-ol (Table 1, Fig. 2). The spectrum of $[(OH)(en)_2Cr(OH)Cr(en)_2(OH)]$-$(ClO_4)_3.2H_2O$ in 1 M $NaClO_4$ without additional base is nearly identical to the spectrum of pure dihydroxo mono-ol in agreement with $pK_{a2} = 7.94$. The spectrum of $[(H_2O)(en)_2$-$Cr(OH)Cr(en)_2(OH)]](ClO_4)_4$ in 1 M NaOH is nearly identical to the spectrum in 0.01 M NaOH, 1 M $NaClO_4$. The small blue-shift (1 nm) of the first absorption band observed in 1 M NaOH is most probably due to medium effects and not to a deprotonation of the mono-ol to a μ-oxo dimer. An upper limit to the acid dissociation constant of the dihydroxo mono-ol is, therefore, estimated as $pK_{a3} > 16$ ($pK_w \simeq 15$ at 0°C).

The equilibria between aquahydroxo mono-ol, diaqua mono-ol, and diol. The equilibria between the diol and the mono-ols at 0 °C were studied spectrophotometrically in the region $650 - 340$ nm. The hydrogen ion concentration was varied from 10^{-3} M to 1.00 M and the ionic strength, $\mu = 1.00 \pm 0.03$ M, was kept constant with sodium perchlorate. In this [H+] region the aquahydroxo mono-ol is partially protonated to diaqua mono-ol, while protonation of the diol does not need to be considered, as mentioned above. The spectra of solutions initially composed of either diol or mono-ol changed with time and became constant within one and a half to three hours. At low acidity one and at high acidity three, well-defined isosbestic points were observed. For each hydrogen ion concentration the final curves and the isosbestic points were identical for solutions initially composed by either diol or mono-ol. The final spectra thus represent an equilibrium mixture between diol, aquahydroxo mono-ol and diaqua mono-ol.

The equilibrium curves for [H+] = 10^{-3} and 5×10^{-3} M were nearly identical corresponding to an equilibrium between diol and aquahydroxo mono-ol alone (see Fig. 1). At higher [H+] a blue-shift of the first absorption band was observed and corresponds to an additional equilibrium involving the diaqua mono-ol. The equilibria which need to be considered are, therefore,

$$[(en)_2Cr(OH)_2Cr(en)_2]^{4+} + H_2O \underset{k_{-1}}{\overset{\overset{\textstyle K_{eq}}{k_1}}{\rightleftharpoons}}$$
$$[(H_2O)(en)_2Cr(OH)Cr(en)_2(OH)]^{4+} \qquad (6)$$

$$[(H_2O)(en)_2Cr(OH)Cr(en)_2(OH)]^{4+} + H^+ \overset{(K_{a1})^{-1}}{\rightleftharpoons}$$
$$[(H_2O)(en)_2Cr(OH)Cr(en)_2(H_2O)]^{5+} \qquad (7)$$

where $K_{eq} = k_1/k_{-1} = $ [aquahydroxo mono-ol]/[diol] and K_{a1} is the first acid dissociation constant of the diaqua mono-ol. K_{eq} and K_{a1} were determined spectrophotometrically as follows. Considering solutions with identical hydrogen ion concentration, we denote the molar absorbancies at the wavelength λ extrapolated back to $t = 0$ and at equilibrium, respectively, as $\varepsilon_0(\lambda)$ and $\varepsilon_{eq}(\lambda)$. Then $\varepsilon_0^D(\lambda)$ and $\varepsilon_0^M(\lambda)$ refer to solutions of diol and mono-ol, respectively. The mol fraction of diol, X, at equilibrium can then be expressed as

$$X = \frac{[Diol]}{[Diol] + [Mono-ol]} = \frac{\varepsilon_{eq}(\lambda) - \varepsilon_0^M(\lambda)}{\varepsilon_0^D(\lambda) - \varepsilon_0^M(\lambda)} \qquad (8)$$

The dependence of X on the hydrogen ion concentration is then expressed by

$$X = \frac{1}{1 + K_{eq}} - \frac{K_{eq}}{K_{a1}(1 + K_{eq})}(X[H^+]) \qquad (9)$$

The expression gives a linear relationship for X against $X[H^+]$. In Fig. 3 such a plot has been made for [H+] = $10^{-3} - 1.00$ M. In the calculation of X, the mean value obtained for the wavelength $\lambda = 550$, 560, and 570 nm was used. From the slope, $-K_{eq}/[K_{a1}(1 + K_{eq})]$, and the intercept, $1/(1 + K_{eq})$, the values $K_{a1} = 0.216$ M and $K_{eq} = 0.835$ were then calculated.
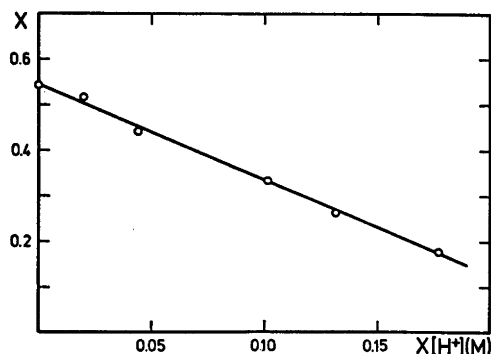

Fig. 3. Spectrophotometric determination of K_{a1} and K_{eq} at 0.8 °C and $\mu = 1.00$ M. See text.

For the medium 1 M $NaClO_4$ (pH = 5 – 6), the equilibrium curves were not well defined as further hydrolysis of unknown character proceeds faster in neutral solutions than in acid solutions. However, using the absorption curves at 7 $t_{\frac{1}{2}}$ for the equilibrium curves, and eqn. (9), which at low [H+] reduces to $K_{eq} = (1 - X)/X$, the value $K_{eq} = 0.91$ was calculated. This value is in reasonable agreement with the more accurate value $K_{eq} = 0.84$ determined above.

Additional spectrophotometric measurements in the media 10^{-3} M $HClO_4$ at 0 °C and 10^{-3} M $HClO_4$, 1 M $NaClO_4$ at 20 °C, respectively, showed identical equilibrium curves for solutions initially composed by either diol or mono-ol. The equilibrium constants calculated for these media using the expression $K_{eq} = (1 - X)/X$ are given in Table 4. The values of $\varepsilon_0^M(\lambda)$ and $\varepsilon_0^D(\lambda)$, ($\lambda = 570$, 560, and 550 nm) were remeasured for each medium and temperature and small differences (up to 3 %) relative to the ε-values measured at $\mu = 1.00$ M and 0 °C were observed.

The kinetics of the equilibrium between mono-ol and diol. The kinetics of the equilibria between the diol and the aquahydroxo and diaqua mono-ols was investigated spectrophotometrically by following the change of the absorbancy of solutions initially composed of either the diol or the mono-ols. The pseudo first-order rate constants, k_{obs}, were obtained by plotting $\log(A_t - A\infty)$ against time [eqn. (1)]. In Table 3, the values of k_{obs} (at $\mu = 1.00$ M and 0.8 °C) are seen to be nearly identical for solutions with identical hydrogen ion concentration, but initially composed of either diol [$k_{obs}(D)$] or mono-ol [$k_{obs}(M)$]. At low hydrogen ion concentration, k_{obs} is almost independent of the hydrogen ion concentration, but as the hydrogen ion concentration increases, a decrease of k_{obs} is observed. As discussed above, the stoichiometry of the reaction can be expressed by eqns. (6) and (7). Neglecting other equilibria, *e.g.* bridge formation and cleavage through a protonated diol, the following rate-law is predicted from eqns. (6) and (7),

$$k_{calc} = k_1 + \frac{K_{a1}}{[H^+] + K_{a1}} \times k_{-1} \qquad (10)$$

where K_{a1} is the first acid dissociation constant of the diaqua mono-ol, and k_1 and k_{-1} are the pseudo first-order and true first-order rate
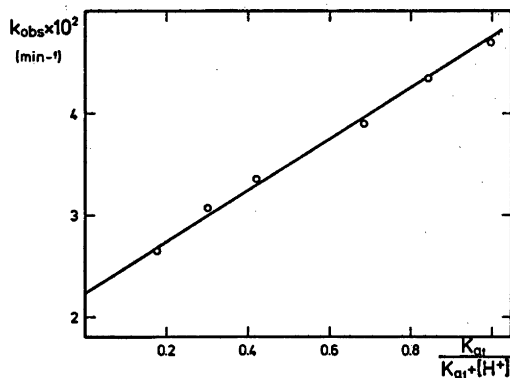

Fig. 4. The observed rate constants for the equilibrium reaction between diol and mono-ol as a function of $K_{a1}/K_{a1} + [H^+])$ at 0.8 °C and $\mu = 1.00$ M ($K_{a1} = 0.216$ M). The solid line represents the calculated values of k_{obs} given in Table 3.

constants, respectively, in eqn. (6). The expression (10) gives a linear relation for k_{obs} against $K_{a1}/(K_{a1} + [H^+])$. Such a plot has been made in Fig. 4 using the $k_{obs}(av)$ values from Table 3 and $K_{a1} = 0.216$ M as found above. From the slope, k_{-1}, and the intercept, k_1, the (pseudo) first-order rate constants are found to be $k_1 = 2.21 \times 10^{-2}$ min^{-1} and $k_{-1} = 2.54 \times 10^{-2}$ min^{-1}. From these values and the relation $K_{eq} = k_1/k_{-1}$, it is found that $K_{eq} = 0.87$, which within the experimental accuracy is in fair agreement with the more accurate value 0.84 as found above.

For the media 10^{-3} M $HClO_4$ at 0.8 °C and 10^{-3} M $HClO_4$, 1 M $NaClO_4$ at 20 °C, respectively, the values of k_{obs} for solutions initially composed of either diol or mono-ol again were found to be nearly identical, as seen in Table 4. The values of k_1 and k_{-1} given in Table 4 are calculated from the expression $k_{obs} = k_1 + k_{-1}$, which is valid for acid solutions with [H+] $\ll K_{a1}$ [see eqn. (10)]. The Arrhenius activation energies $E_a(k_1) = 19.6$ kcal/mol and $E_a(k_{-1}) = 20.7$ kcal/mol were then calculated from the rate constants at $\mu = 1.00$ M given in Table 4.

DISCUSSION

The μ-hydroxo bridged structure proposed for the three mono-ols is strongly supported by the values of the ligand field parameter Δ of

these species. From the spectral data given in Table 1, the Δ values for the diaqua mono-ol, the aquahydroxo mono-ol, and the dihydroxo mono-ol, respectively, are calculated to 19.88, 19.42, and 19.00 kK. In agreement with the average environment rule the Δ value for the aquahydroxo mono-ol within the experimental accuracy is equal to the average of the Δ values of the diaqua mono-ol and the dihydroxo mono-ol ($\Delta_{obs} = 19.42$ kK and $\Delta_{calc} = 19.44$ kK). The observed decrease in Δ by the replacement of H_2O by OH^- follows the spectrochemical series. Furthermore, the replacement of one H_2O by OH^- per Cr(III), is seen to correspond to a decrease of Δ by 0.88 kK. This is in excellent agreement with the corresponding value 0.86 kK obtained from the Δ values of cis-$[Cr(en)_2(H_2O)_2]^{3+}$ and cis-$[Cr(en)_2(OH)_2]^+$ ($\Delta = 20.58$ kK and 18.87 kK, respectively).[28]

The equilibrium constant, K_{eq}, for the equilibrium between meso-$[(en)_2Cr(OH)_2Cr(en)_2]^{4+}$ and $[(H_2O)(en)_2Cr(OH)Cr(en)_2(OH)]^{4+}$ is nearly 40 times greater than K_{eq} for the corresponding equilibrium between $[(H_2O)_4Cr(OH)_2Cr(H_2O)_4]^{4+}$ and $[(H_2O)_5Cr(OH)Cr(H_2O)_4(OH)]^{4+}$ ($K_{eq} = 0.02$ at 25 °C in 2 M $LiClO_4$, calculated from the data given in Ref. 21). In both systems the variation of K_{eq} with temperature is small. In the ethylenediamine system the standard enthalpy change, $\Delta H°$, for the cleavage reaction of diol to aquahydroxo mono-ol was calculated from the data in Table 4 to be $\Delta H° = -0.7$ kcal/mol (1 M $NaClO_4$). The influence of ionic strength on K_{eq} is seen from Table 4 to be very small as would be expected for equilibria only involving reactions between one ion and one neutral molecule. It is noted that the small decrease of K_{eq} with increasing ionic strength corresponds closely to the change in water activity ($a_{H_2O} = 52.9$ M in 1 M $NaClO_4$ and $a_{H_2O} = 55.5$ M in 5×10^{-3} M $NaClO_4$ at 20 °C).[29]

The equilibrium between diol and aquahydroxo mono-ol is established very fast and k_1 as well as k_{-1} are several orders greater than the rate constant for water exchange in $[Cr(H_2O)_6]^{3+}$.[30] Furthermore, k_1 is about 10^2 times greater than the corresponding rate constant for the aqua diol, $k_1(aq) = 9 \times 10^{-4}$ min^{-1} at 25 °C.[21] The corresponding value for the phenanthroline diol has been estimated to be 2×10^{-3} min^{-1} at 20 °C.[20] At present we have no clear understanding why k_1 apparently

is so much greater when ethylenediamine is the non-bridging ligand. In connection with the acid cleavage of diols it has been discussed to which extent the cleavage of the bridge to form mono-ol occurs through direct aquation or through an intermediate involving protonation of the hydroxo bridge. The observation that no hydrogen ion dependent term in the $[H^+]$ region $10^{-3} - 1.0$ M was found for the ring-opening reaction of the ethylenediamine diol supports the mechanism with direct aquation as proposed for the phenanthroline diol and the aqua diol.[19—21]

The large value of k_{-1} is probably due to proximity effects. As the k_{-1} path corresponds to an intramolecular nucleophilic attack by coordinated OH^-, one would expect a great enhancement in reactivity relative to a corresponding intermolecular nucleophilic attack. Analogously the ring-closure of $[(H_2O)_5Cr(OH)Cr(H_2O)_4(OH)]^{4+}$ to form diol is reported to be fast ($k_{-1} = 0.05$ min^{-1}, 25 °C).[21]

The observation that the $[(H_2O)(en)_2Cr(OH)Cr(en)_2(H_2O)]^{5+}$ cation is approximately a 10^2 times stronger acid than the cis-aqua erythro ion, $[(NH_3)_5Cr(OH)Cr(NH_3)_4(H_2O)]^{5+}$ ($pK_a = 3.5$ in 1 M $NaNO_3$ and 2.8 in 0.14 M $NaClO_4$ at at 25 °C)[21,4] is hardly explained in terms of the difference in the electronic properties of the N-ligators. We suggest that the low pK_{a1} of the diaqua mono-ol is due to a strong hydrogen-bonded stabilization of the corresponding base, aquahydroxo mono-ol, as outlined below.
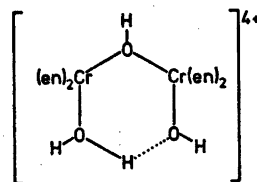
In a following paper in this series it is shown that, analogously to the meso isomer, the racemic isomer of the $[(en)_2Cr(OH)_2Cr(en)_2]^{4+}$ cation very fast gives an equilibrium mixture of diol and mono-ol.

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