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Binuclear Complexes of Chromium(III). II. Synthesis and Properties of the Racemic Isomers of μ-Hydroxo and Di-μ-hydroxo Binuclear Complexes of Chromium(III) with Ethylenediamine as a Ligand

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The new binuclear ions Δ,Δ-Λ,Λ-$[(en)_2Cr(OH)_2Cr(en)_2]^{4+}$ (diol) and Δ,Δ-Λ,Λ-$[(H_2O)(en)_2Cr(OH)Cr(en)_2(OH)]^{4+}$ (aquahydroxo monool) have been prepared from the *meso* isomer Δ,Λ-$[(en)_2Cr(OH)_2Cr(en)_2]^{4+}$ and isolated as various salts. The *racemic* diol equilibrates rapidly in aqueous solution with the aquahydroxo monool and the equilibrium constant K_{eq} = [aquahydroxo monool]/[diol] was determined spectrophotometrically to be 0.240 at 0.8 °C and 0.227 at 20 °C at an ionic strength of 1.00 M. The acid dissociation constants, K_{a1} and K_{a2}, of the diaqua monool, Δ,Δ-Λ,Λ-$[(H_2O)(en)_2Cr(OH)Cr(en)_2(OH_2)]^{5+}$ were determined spectrophotometrically ($pK_{a1} = 0.72$ at 0.8 °C and 0.57 at 20 °C) and potentiometrically ($pK_{a2} = 6.87$ at 20 °C).

The kinetics of the equilibration between diol and monool were studied spectrophotometrically in the pH range $0 \leq pH \leq 4$, and using the pH-stat technique in the pH range $7 \leq pH \leq 9$. The rate expressions are $-d[diol]/dt = d[monool]/dt = k_1[diol] - k_{-1}K_{a1}/(K_{a1}+[H^+])[monool]$ for the acid region and $-d[diol]/dt = d[monool]/dt = k_1[diol] - k_{-1} \times [H^+]/(K_{a2}+[H^+])[monool]$ for the basic region, where $k_1 = 2.53 \times 10^{-3}$ s^{-1} (20 °C) is the pseudo first-order rate constant for the reaction of diol to give aquahydroxo monool and $k_{-1} = 1.12 \times 10^{-2}$ s^{-1} (20 °C) is the true first-order rate constant for the reverse reaction. From these data, together with additional kinetic data determined spectrophotometrically at 0.8 °C, the activation parameters $E_a(k_1) = 87$ kJ/mol and $E_a(k_{-1}) = 90$ kJ/mol were calculated.

The equilibrium constant, K_{isom} = [racem]/[meso], for the equilibrium between the *racemic* and the *meso* isomers of the cation $[(HO)(en)_2Cr(OH)Cr(en)_2(OH)]^{3+}$ was estimated to be 4 ± 2 in aqueous ethylenediamine (7 M) at 45 °C.

When heated (140 °C, 1 h) in the solid state, the bromide salts of the *racemic* diol and of the *racemic* aquahydroxo monool isomerize to give *meso* diol.

In the first paper[1] in this series, the binuclear cation Δ,Λ-$[(en)_2Cr(OH)_2Cr(en)_2]^{4+}$(diol) in acid solution was shown to rapidly attain equilibrium with the corresponding monohydroxo bridged cations, Δ,Λ-$[(H_2O)(en)_2Cr(OH)Cr(en)_2(OH)]^{4+}$ (aquahydroxo monool) and Δ,Λ-$[(H_2O)(en)_2Cr(OH)Cr(en)_2(OH_2)]^{5+}$ (diaqua monool). The thermodynamics and kinetics of the equilibration reaction between monool and diol were studied in the $[H^+]$ region $10^{-4} \leq [H^+] \leq 1.0$ M and no evidence for an acid-catalyzed path was obtained. X-Ray structure analyses of several salts of the diol, Δ,Λ-$[(en)_2Cr(OH)_2Cr(en)_2]X_m.nH_2O$ ($X_m.nH_2O = (ClO_4)_2Cl_2.2H_2O, (S_2O_6)_2, Cl_4.2H_2O$ and $Br_4.2H_2O$)[2-5] and of one salt of the monool,[6] Δ,Λ-$[(HO)(en)_2Cr(OH)Cr(en)_2(OH)](ClO_4)_3.H_2O$, have recently been reported.

The present paper concerns the isomeric forms of the latter cations, *i.e.* the *racemic* diol, Δ,Δ-Λ,Λ-$[(en)_2Cr(OH)_2Cr(en)_2]^{4+}$, and the corresponding *racemic* monools. A preliminary reported has been published.[7]

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RESULTS AND DISCUSSION

Preparations. When *meso* diol chloride, Δ,Λ-$[(en)_2Cr(OH)_2Cr(en)_2]Cl_4.2H_2O$, is dissolved in aqueous ethylenediamine (~ 7 M) at 45 °C, it gives initially *meso* dihydroxo monool which on further heating equilibrates with its racemic isomers, Δ,Δ and Λ,Λ. Both isomers were isolated by a fractional precipitation procedure, giving Δ,Δ-Λ,Λ-$[(H_2O)(en)_2Cr(OH)Cr(en)_2(OH)]Br_4.H_2O$ and Δ,Λ-$[(en)_2Cr(OH)_2Cr(en)_2]Br_4.2H_2O$, respectively, in the yields 42 and 14 %.

When the above procedure was repeated, but with *racemic* aquahydroxo monool bromide substituted for *meso* diol, the yields of *racemic* monool and of *meso* diol were 43 and 10 %, respectively, which within the experimental accuracy is identical to those given above. This result clearly shows that the basic product solution has attained equilibrium with respect to these isomers.

Since the isolated salts are sparingly soluble under the experimental conditions – *meso* diol bromide is nearly insoluble in excess of bromide – the yields given above can be taken as reasonable estimates for the actual concentrations of the dihydroxo isomers in the basic equilibrium solution.

As a rough estimate for the equilibrium constant, $K_{isom} = [racem]/[meso]$, referring to the dihydroxo monools, we therefore get $K_{isom} = 4 \pm 2$, which is significantly larger than the statistically expected value of one.

The role of the free amine in the equilibration procedure described above is to maintain a high and relatively constant pH (10 – 11) of the reaction mixture and it was found that triethylamine could be used instead of ethylenediamine.

The *racemic* aquahydroxo monool equilibrates rapidly in aqueous solution with its corresponding *racemic* diol, and the latter cation was isolated from equilibrated solution as the perchlorate salt in 72 % yield by precipitation with a large excess of sodium perchlorate. The bromide salt of the diol was isolated analogously (50 %).

Several unsuccessful attempts have been made to separate these binuclear cations into their enantiomers, *i.e.* Δ,Δ and Λ,Λ. A major complication is the fact that classical resolving agents such as tartrate, camphor sulfonate *etc.* all react with the chromium(III) complexes forming, *e.g.*, μ-carboxylato-O,O-μ-hydroxo binuclear compounds.[8-10] Resolution of these carboxylato-bridged species with subsequent (stereospecific) reformation of diol would clearly be a possible route, and is now being explored.

Spectra. The absorption spectra of aqueous solutions of salts of the diol, Δ,Δ-Λ,Λ-$[(en)_2Cr(OH)_2Cr$-

Table 1. Spectral data at 0.8 °C.

Sample	Medium[a]	$(\varepsilon,\lambda)_{max}$	$(\varepsilon,\lambda)_{max}$
Δ,Δ-Λ,Λ-$[(en)_2Cr(OH)_2Cr(en)_2](ClO_4)_4$	0.001 M $HClO_4$, 1 M $NaClO_4$	(190,538.5)	(102,384)
	1 M $HClO_4$	(188,538.5)	(101,384)
Δ,Δ-Λ,Λ-$[(H_2O)(en)_2Cr(OH)Cr(en_2(OH)]Br_4.H_2O$	0.0001 M $HClO_4$, 1 M $NaClO_4$	(162,515)	(128,381)
	0.01 M NaOH, 1 M $NaClO_4$	(163,522)	(141,380)
	1 M NaOH	(163,522.5)	(145,380)
Δ,Δ-Λ,Λ-$[(H_2O)(en)_2Cr(OH)Cr(en)_2(H_2O)]^{5+}$	–	(163,503)[b]	(102,379)[b]

[a] The concentration of the complexes was in all cases $\sim 4 \times 10^{-3}$ M. [b] Calculated, see text.

Table 2. Thermodynamic data for *meso* and *racemic* monools and diols. Ionic strength 1.00 M, (H^+, Na^+), ClO_4^-. pK_{a1} and K_{eq} determined spectrophotometrically and pK_{a2} determined potentiometrically.

Isomer	Temp., °C	pK_{a_1}	pK_{a_2}	K_{eq}	Ref.
meso	0.8	0.67	7.94	0.835	1
racemic	0.8	0.72	–	0.240	This work
meso	20.0	–	–	0.763	1
racemic	20.0	0.57	6.87	0.227	This work

$(en)_2]^{4+}$, or salts of the aquahydroxo monool, Δ,Δ-Λ,Λ-$[(H_2O)(en)_2Cr(OH)Cr(en)_2(OH)]^{4+}$, changed rapidly with time owing to rapid equilibration between monool and diol. The spectra of diol and of aquahydroxo monool were thus obtained by extrapolation of these absorption curves back to the time of dissolution. The spectra of the diol in 10^{-3} M $HClO_4$, 1 M $NaClO_4$ and in 1 M $HClO_4$ are identical (see Table 1), showing that protonation of the diol can be ignored in this $[H^+]$ region. This is supported by the thermodynamic and kinetic results (see below) and is consistent with results obtained recently for the *meso* system.[1]

The spectrum of Δ,Δ-Λ,Λ-$[(H_2O)(en)_2Cr(OH)Cr(en)_2(OH)]Br_4.H_2O$ in 10^{-4} M $HClO_4$, 1 M $NaClO_4$ (Table 1) represents the spectrum of pure aquahydroxo monool cation, as can be seen from the pK_a values given in Table 2. The spectrum of the diaqua monool cation was calculated from the spectra of monool in 1 M $HClO_4$ and 10^{-3} M $HClO_4$, 1 M $NaClO_4$ (0.8 °C) using the spectrophotometrically determined value for pK_{a1} (Table 2).

The spectra of 4×10^{-3} M solutions of Δ,Δ-Λ,Λ-$[(H_2O)(en)_2Cr(OH)Cr(en)_2(OH)]Br_4.H_2O$ in 0.01 M NaOH, 0.99 $NaClO_4$ and in 1.00 M NaOH are nearly identical as seen in Table 1 and thus represent the spectrum of the dihydroxo monool cation. This result implies that deprotonation of the hydroxo bridge to form an oxo-bridged cation can be ignored under these conditions, as has been found for the *meso* isomer.[1]

Solid state reactions. It was shown previously that the perchlorate salt of the *meso* aquahydroxo monool rapidly forms *meso* diol in the solid state at room temperature and, as shown in the present work, the bromide salt is also unstable at room temperature. The properties of the corresponding *racemic* bromide salt are quite different in that respect, as discussed below.

Solid *racemic* aquahydroxo monool, Δ,Δ-Λ,Λ-$[(H_2O)(en)_2Cr(OH)Cr(en)_2(OH)]Br_4.H_2O$, is stable for months at room temperature. When heated to 115 °C, the solid salt loses the crystal water, but neither formation of diol nor isomerization occur at this temperature. At higher temperatures (125–135 °C) another mol of water is lost and heating at 140 °C for 1 h gave an almost quantitative (95 %) conversion to *meso* diol bromide.

Solid Δ,Δ-Λ,Λ-$[(en)_2Cr(OH)_2Cr(en)_2]Br_4.4H_2O$ loses the 4 H_2O in the temperature range 50–60 °C. At higher temperatures isomerization to *meso* diol takes place, but heating at 140 °C for 1 h gave only a low yield (20 %) of *meso* diol.

The conversion of *racemic* monool bromide to *meso* diol bromide by heating in the solid state can be explained as a consequence of a larger lattice energy for the *meso* bromide salt than for the *racemic* bromide salt. However, the much lower yield of *meso* diol formed by heating *racemic* diol is surprising and might imply that two different mechanisms are operating. That lattice energy can be of major importance in this type of conversion is illustrated by the fact that *meso* monool bromide at room temperature is converted to the *meso* diol within hours, whereas *racemic* monool bromide under these conditions is stable for months; in solution both cations form diol at a comparable rate.

Assignment of structures. The proposed hydroxo- and dihydroxo-bridged structures follows from the observed acid-base properties, which clearly establish the presence of two acidic terminal aqua groups in the monool and the absence of terminal aqua groups in the diol. The positions of the first ligand field bands are identical, within 1 nm, to those for the *meso* compounds,[1] except for the *racemic* dihydroxo monool, for which the band is blueshifted 4 nm.

Salts of *racemic* diol dissolved in strongly basic solution (1 M NaOH) give a blue solution of the deprotonated μ-hydroxo-μ-oxo complex. This is also seen for the *meso* diol salts and seems to be a general feature of amine chromium(III) diols.[1,11,12] The ESR spectra[7] of the *racemic* compounds are also very similar to those of the respective *meso* compounds.

Another observation which supports the proposed structures is that the isomers react similarly with carboxylic acids giving the corresponding isomers of μ-carboxylato-*O,O*-μ-hydroxo complexes.[8] A similar result was found for the reaction with sulfuric acid, producing μ-sulfato-*O,O*-μ-hydroxo complexes.[9,10,13]

Some properties which clearly distinguish between *racemic* and *meso* isomers are the X-ray powder diffraction patterns (no similarity for salts of the diols with anions ClO_4^- or Br^- and for the monools with Br^-) and IR spectroscopy (significant differences in the region 1700–300 cm^{-1} for each pair of bromides). Furthermore, the solubilities are also very different in some instances, *e.g.*, the bromide salt of *racemic* diol is considerably more soluble in water than *meso* diol bromide. Other similarities and dissimilarities relevant to the discussion above are mentioned below.

The equilibrium between monool and diol. The thermodynamics and kinetics for the equilibrium between monool and diol were studied spectrophotometrically in the pH region $0 \leq pH \leq 4$ and potentiometrically in the region $6.9 \leq pH \leq 8.6$.

The equilibrium between monool and diol at 0.8 °C and at 20 °C was studied spectrophotometrically in the region 650 – 340 nm. The hydrogen ion concentration was varied from 10^{-4} to 1.00 M and in this $[H^+]$ region the aquahydroxo monool is partially protonated to diaqua monool, while protonation of the diol does not need to be considered, as mentioned above. The spectra of solutions initially containing either diol or monool changed with time and became constant within $1\frac{1}{2}-3$ h (0.8 °C) and 6 – 12 min (20 °C), respectively. For each hydrogen ion concentration the final spectral curves and the isosbestic points were identical for solutions initially prepared from either diol or monool. The final spectra thus represent those of an equilibrium mixture of diol, aquahydroxo monool and diaqua monool.

The equilibria which express the stoichiometry are therefore as given in eqns. (1) and (2), where

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

$$[(H_2O)(en)_2Cr(OH)Cr(en)_2(H_2O)]^{5+} \overset{K_{a1}}{\rightleftarrows} [(H_2O)(en)_2Cr(OH)Cr(en)_2(OH)]^{4+} + H^+ \quad (2)$$

$K_{eq} = k_1/k_{-1} = $ [aquahydroxo monool]/[diol] and K_{a1} is the first acid dissociation constant of diaqua monool. From the $[H^+]$ dependence of the molar absorbancies at the time of dissolution and at equilibrium the constants K_{eq} and K_{a1} were calculated as recently described for the *meso* system.[1] The results are given in Table 2.

Pseudo first-order rate constants, k_{obs}, were calculated using eqn. (7) and are shown in Table 3. The values of k_{obs} are seen to be nearly identical for solutions with identical hydrogen ion concentrations, but initially containing either diol $[k_{obs}(D)]$ or monool $[k_{obs}(M)]$. At low hydrogen ion concentration, k_{obs} is almost independent of $[H^+]$, but as the latter is increased a decrease in k_{obs} is observed. As discussed above, the stoichiometry of the reaction can be expressed by eqns. (1) and (2). Neglecting other equilibria, *e.g.* bridge formation and cleavage through a protonated diol, the rate-law given in eqn. (3) is predicted from eqns. (1) and (2), where

$$k_{calc} = k_1 + \frac{K_{a1}}{[H^+]+K_{a1}} k_{-1} = k_{-1}\left(K_{eq} + \frac{K_{a1}}{[H^+]+K_{a1}}\right) \quad (3)$$

k_1 and k_{-1} are the pseudo first-order and true first-order rate constants, respectively, in eqn. (1). The expression predicts that a plot of k_{obs} against $[K_{eq} + K_{a1}/([H^+]+K_{a1})]$ should give a straight line passing through the origin. Such a plot has been

Table 3. Observed and calculated rate constants for the equilibrium between the monools and the diol based on spectrophotometric measurements. Ionic strength 1.00 M, (H^+, Na^+), ClO_4^-. k_{calc} from eqn. (3).

Temp. °C	C_{HClO_4} mol/l	$10^3 \times k_{obs}(D)$ s^{-1}	$10^3 \times k_{obs}(M)$ s^{-1}	$10^3 \times k_{obs}(av)$ s^{-1}	$10^3 \times k_{calc}$ s^{-1}
0.8	10^{-4}	1.08	1.05	1.07	1.06
–	10^{-3}	0.99	1.02	1.00	1.05
–	0.100	0.79	0.74	0.77	0.77
–	0.250	0.55	0.53	0.54	0.58
–	0.500	0.45	0.42	0.44	0.44
–	0.750	0.39	0.37	0.38	0.38
–	1.000	0.36	0.37	0.37	0.34
20.0	10^{-4}	12.3	13.1	12.7	13.7
–	10^{-3}	12.5	13.3	12.9	13.6
–	0.101	11.5	10.8	11.2	10.6
–	0.326	7.7	7.7	7.7	7.6
–	0.485	6.5	6.7	6.6	6.5
–	0.750	6.1	6.0	6.0	5.5
–	1.007	5.4	5.7	5.6	4.9

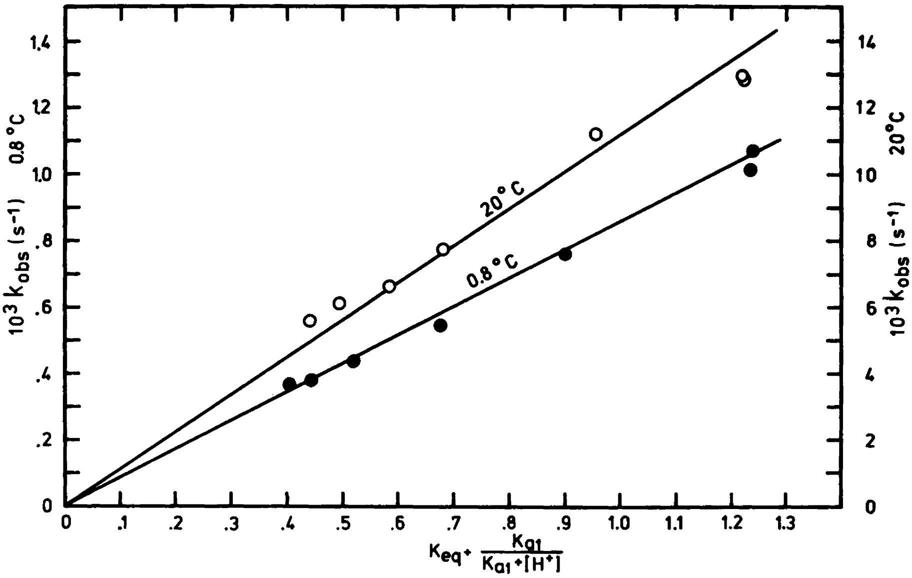

Fig. 1. The observed rate constants for the equilibrium reaction between monool and diol as a function of $K_{eq}+K_{a1}/(K_{a1}+[H^+])$, where K_{eq} and K_{a1} are taken from Table 2. The solid lines represent the calculated values of k_{obs} given in Table 3.

made in Fig. 1 for each temperature, using the k_{obs}(av) values given in Table 3 and K_{a1} and K_{eq} values determined spectrophotometrically as mentioned above (Table 2). From the slope, k_{-1}, and the relation $k_1=K_{eq}k_{-1}$, the (pseudo) first-order rate constants were calculated and are given in Table 4. In Table 3 values of k_{obs} and k_{calc} are compared and are seen to agree well, particularly at 0.8 °C. This result implies that the kinetic data are consistent with the thermodynamically determined equilibrium constants.

The Arrhenius activation energies E_a $(k_1)=87$ kJ/mol and E_a $(k_{-1})=90$ kJ/mol were then calculated from the rate constants given in Table 4.

The second acid dissociation constant, K_{a2}, for the diaqua monool, defined by the equilibrium (4)

$$[(H_2O)(en)_2Cr(OH)Cr(en)_2(OH)]^{4+} \rightleftarrows [(HO)(en)_2Cr(OH)Cr(en)_2(OH)]^{3+} + H^+ \quad (4)$$

was determined by glass-electrode measurements, essentially as described previously for the *meso* system[1] (Table 2).

The kinetics and thermodynamics of the equilibrium between diol and monool were studied in the pH region 7–9, using the pH-stat technique. All measurements were made on solutions initially prepared from diol and as the equilibration reaction proceeded a constant pH was maintained by addition of base. The pseudo first-order rate constants,

Table 4. Kinetic parameters for monool-diol equilibration of *meso* and *racemic* isomers. Ionic strength 1.00 M, (H^+, Na^+), ClO_4^-. All parameters determined spectrophotometrically.

Isomer	Temp. °C	$10^3\times k_1$ s^{-1}	$10^3\times k_{-1}$ s^{-1}	$E_a(k_1)$ kJ/mol	$E_a(k_{-1})$ kJ/mol	Ref.
meso	0.8	0.368	0.423	82	87	1
racemic	0.8	0.205	0.853	87	90	This work
meso	20.0	3.92	5.13	–	–	1
racemic	20.0	2.53	11.2	–	–	This work

Table 5. Observed and calculated rate constants at 20 °C and ionic strength 1.00 M. k_{obs} obtained by pH-stat technique. k_{calc} obtained using eqn. (6) with parameter values taken from Table 2 and Table 4.

pH	$10^3 \times k_{obs}$ s^{-1}	$10^3 \times k_{calc}$ s^{-1}
6.88	8.2	8.1
7.21	6.4	6.1
7.33	6.0	5.4
7.73	4.1	3.9
7.81	3.9	3.7
8.64	3.0	2.7

k_{obs}, were obtained by plotting ln $(B_\infty - B_t)$ against t, where B_t and B_∞ are mmol base added at time t and at equilibrium [eqn. (8)]. Since the diol itself has no buffer capacity in this pH region B_t at $t=0$ is negligible. Such plots were linear for at least three half-lives, and values of k_{obs} are given in Table 5. In this pH region the stoichiometry of the equilibrium solutions is defined by the equilibrium between the diol and the aquahydroxo monool and by the acid-base equilibrium between aquahydroxo and dihydroxo monool, eqns. (1) and (4). These two relationships lead to the expression (5), where

$$\frac{1}{x} = 1 + \frac{1+K_{eq}}{K_{a2}K_{eq}} \times [H^+] \tag{5}$$

$x = B_\infty/$(mmol complex) is the mol fraction of dihydroxo monool at equilibrium. Eqn. (5) predicts a linear plot of x^{-1} against $[H^+]$ with intercept 1. Such a plot has been made in Fig. 2. From the slope, $(1+K_{eq})/(K_{a2}K_{eq})$, the equilibrium constant K_{eq} can be determined when K_{a2} is known. Using the value for K_{a2} as determined above (Table 2), we obtain $K_{eq}=0.25$, which is in fair agreement with the more reliable value of 0.23 determined spectrophotometrically (see Table 2).

As seen above, the stoichiometry at equilibrium can be described by eqns. (1) and (4). Neglecting other equilibria, *e.g.* bridge cleavage and formation through a μ-hydroxo-μ-oxo complex, the rate-law (6) is predicted from eqns. (1) and (4).

$$k_{calc} = k_1 + \frac{[H^+]}{[H^+]+K_{a2}} \times k_{-1} \tag{6}$$

The values of k_{calc} given in Table 5 were then obtained using the expression above with the values for K_{a2} (Table 2) and for k_1 and k_{-1} (Table 4) as determined above. The values of k_{calc} and k_{obs} are seen to be in satisfactory agreement considering the fact that k_{calc} values have been obtained com-

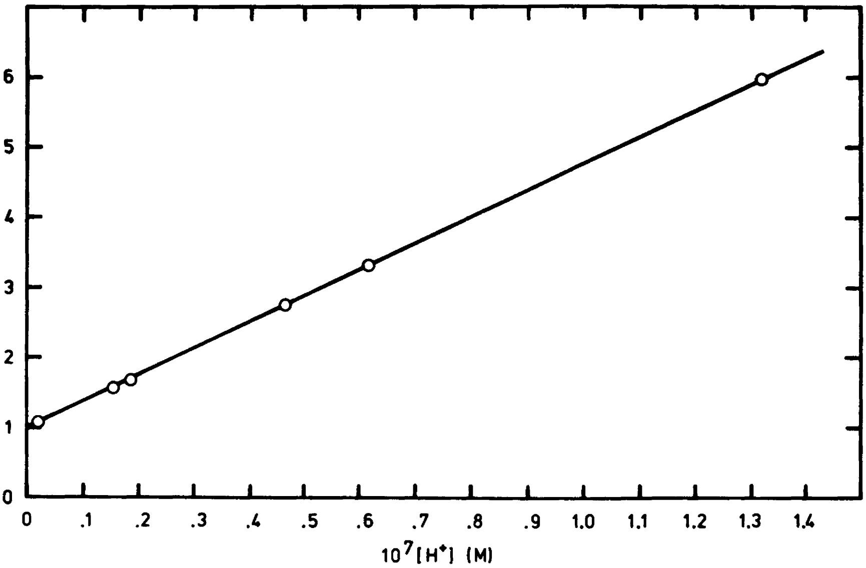

Fig. 2. Determination of the equilibrium constant K_{eq} from the pH-stat data in the region $6.9 \leq pH \leq 8.6$ at 20 °C. See text.

pletely independently of the kinetic data in this pH region. These results imply that the equilibration reaction between monool and diol in the entire pH region 0–9 occurs through the equilibrium between aquahydroxo monool and diol (eqn. (1)), with no significant acid- or base-catalyzed path.

Comparison between the meso *and the* racemic *systems.* As might have been anticipated, the values of the equilibrium constants for the *racemic* isomers are rather similar to those for the *meso* isomers. Both isomers of the diaqua monool are strongly acidic, and this surprising result (pK_{a1} 3 units lower than for the parent mononuclear complexes) has been explained in terms of a strong hydrogen-bond stabilization of the aquahydroxo monool relative to the diaqua monool.[1,6]

The second acid dissociation constants, pK_{a2}, for the two isomers have been determined at different temperatures (Table 2) and a direct comparison therefore cannot be made. Since the $\Delta H°$ values for both these reactions are probably positive, the values at a given temperature must be rather similar.

The value of K_{eq} decreases by a factor 3.6 on going from the *meso* to the *racemic* system. The standard enthalpy change, $\Delta H°$, for the cleavage reaction of diol to give aquahydroxo monool is -3 kJ for the *meso* system,[1] and from the data in Table 2 a value of -2 kJ is calculated for the *racemic* system. Kinetically, the difference in K_{eq} for the two systems corresponds to differences in both rate constants, and we have the rough result $k_1(meso) \simeq 2k_1(racem)$ and $k_{-1}(meso) \simeq 0.5\ k_{-1}(racem)$. The rate constants for the *meso* system and the *racemic* system are therefore of the same order of magnitude and from Table 4 it is seen that the activation energies associated with both rate constants are very similar.

From the results discussed above it is concluded that the thermodynamic and kinetic parameters for the two systems are very similar, which is a reasonable result since we are dealing with diastereoisomers.

The rate constants k_1 and k_{-1} are both unusually large compared with rate constants for analogous monomeric chromium(III) complexes. Strain in the bridge and the proximity effect, respectively, may explain the enhanced values for k_1 and k_{-1}, as recently discussed for the *meso* system.[1]

EXPERIMENTAL

Materials. Salts of the *meso* diol were prepared by published methods.[11] Sodium perchlorate and 70 % perchloric acid with the description *puriss. p.a.* were purchased from Fluka AG. Sodium hydroxide solutions were prepared from 'Titrisol' ampoules purchased from Merck. All other chemicals were of analytical grade. CO_2-free distilled water was used for all spectrophotometric and potentiometric measurements.

Instruments. A Zeiss DMR 21 spectrophotometer was used for all spectrophotomeric measurements in the visible region. For the spectrophotometric data given above the molar decadic absorption coefficient ε is given in $1\ mol^{-1}\ cm^{-1}$ and the wavelength λ in nm. The molarity of solutions of the dimers is in all cases defined in terms of the number of mol of dimer rather than 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 in conjunction with a PHM 61 digital pH-meter (Radiometer, Copenhagen). The saturated potassium chloride electrolyte in the calomel electrode was replaced with 1 M sodium chloride in order to avoid precipitation of $KClO_4$ in the boundary between the medium and the electrode. The pH-stat instrument consisted of the above-mentioned pH-meter in conjunction with a TTT60 titrator and an ABU12 automatic burette (Radiometer, Copenhagen).

Powder X-ray diffraction diagrams were obtained using a Guinier powder camera with Cu$K\alpha$ radiation.

The thermogravimetric measurements were made by Solveig Kallesøe, Chemistry Dept. I, H. C. Ørsted Institute, University of Copenhagen.

Analysis. Chromium analyses by atomic absorption spectrophotometry were performed by Karen Jørgensen, Chemistry Dept. I, H. C. Ørsted Institute. C, H, N, Br, and Cl analyses were performed by the microanalytical laboratory at the H. C. Ørsted Institute.

Preparations

1. Δ,Δ-Λ,Λ-*Aquatetrakis(ethylenediamine)-μ-hydroxohydroxodichromium(III) bromide*, Δ,Δ-Λ,Λ-$[(H_2O)(en)_2Cr(OH)Cr(en)_2(OH)]Br_4.H_2O$. Δ,Λ-$[(en)_2Cr(OH)_2Cr(en)_2]Cl_4.2H_2O$ (7 g, 12.6 mmol) was added to a warm (45 °C) mixture of ethylenediamine (15 ml) and water (20 ml). The suspension was kept at 45 °C with stirring for 45 min. The salt dissolved completely within 5–10 min and the colour of the solution shifted to red, owing to the formation of the μ-hydroxobis[bis(ethylenediamine)-hydroxochromium(III)] ion. To the resulting red

solution was added water (20 ml). The solution was cooled in ice for 15 min, and 63 % hydrobromic acid (15 ml) was then added in portions with cooling and vigorous stirring. During the addition the temperature was kept below 20 °C. The solution was cooled to 5 °C and further 63 % hydrobromic acid (12 ml) was added portionwise within 20 min, but now the temperature was kept at 5 °C. After a further 5 min the red precipitate was filtered, washed with cold 50 % ethanol, 96 % ethanol and finally with ether. Drying in air yielded 5.0 g of crude aquahydroxo monool bromide. (From the mother liquor *meso* diol bromide can be isolated as described later.)

The crude product of *racemic* aquahydroxo monool bromide is contaminated with a small amount of *meso* diol bromide and was purified as follows: To the crude product (5.0 g) was added cold (10 °C) 0.4 M NaOH (12.5 ml) and a residue of the sparingly soluble *meso* diol bromide (0.6 g) was filtered off. To the filtrate was immediately added an ice-cold mixture of 1.2 M HBr (5 ml) and a saturated (at 20 °C) solution of NaBr (2.5 ml) with cooling in ice and stirring. Precipitation of the *racemic* aquahydroxo monool salt began immediately, and the product was filtered off after 3 min, washed three times with 96 % ethanol (25 ml) and then with ether. Yield 3.9 g (42 % based on *meso* diol chloride) of a pure product. Anal. $[(H_2O)(en)_2Cr(OH)Cr(en)_2(OH)]Br_4.H_2O$: Cr, C, H, N, Br.

The mother liquor from the isolation of crude *racemic* aquahydroxo monool was left for 2 h at room temperature and during this time equilibration between the aquahydroxo monools and their corresponding diols was attained and the sparingly soluble bromide salt of *meso* diol precipitated as a nearly pure salt (yield 0.7 g). The total amount of recovered *meso* diol is therefore 1.3 g corresponding to 14 %.

The preparation was repeated substituting triethylamine (15 ml) for ethylenediamine. The conditions were otherwise as above, except that only half the amount of hydrobromic acid was added. The yield was 2.5 g (33 %) of crude *racemic* aquahydroxo monool.

Visible spectral data in different media are given in Table 1. The solid salt is stable for months at room temperature but above 130 °C it reacts to give *meso* diol bromide (see below). The infrared spectra and X-ray powder diffraction diagrams of this salt and of Δ,Λ-$[(H_2O)(en)_2Cr(OH)Cr(en)_2(OH)]Br_4.aq$, respectively, were entirely different.

2. Δ,Δ-Λ,Λ-*μ-Hydroxobis[bis(ethylenediamine)chromium(III)] perchlorate*, Δ,Δ-Λ,Λ-$[(en)_2Cr(OH)_2Cr(en)_2](ClO_4)_4$. Δ,Δ-Λ,Λ-$[(H_2O)(en)_2Cr(OH)Cr(en)_2(OH)]Br_4.H_2O$ (5 g, 6.8 mmol) was added to a saturated solution of sodium perchlorate (25 ml), and the suspension was stirred at room temperature for 15 min. Within a few minutes the colour of the suspension changed to violet, owing to the precipitation of Δ,Δ-Λ,Λ-$[(en)_2Cr(OH)_2Cr(en)_2](ClO_4)_4$. The suspension was cooled in ice for 20 min and filtered. The product was washed with 96 % ethanol. Yield 3.8 g (72 %).

The crude product (2.5 g) was dissolved in water (8 ml), and the filtered solution was added to a supersaturated solution (25 °C) of sodium perchlorate (30 ml, saturated at 35 °C) containing 1 drop of 12 M $HClO_4$. After standing for 10 min the mixture was cooled in ice for 20 min. The purple product was filtered off and washed three times with 96 % ethanol (10 ml) and then with ether. Yield 2.0 g (80 %). A 10 % aqueous solution of this salt gives no precipitate with 0.1 M $AgNO_3$. The sample reprecipitated twice was pure. Anal. $[(en)_2Cr(OH)_2Cr(en)_2](ClO_4)_4$: Cr, C, H, N, Cl.

Visible spectral data in different media are given in Table 1. The solid salt is stable for months at room temperature. The X-ray powder diffraction diagrams of this salt and of Λ,Δ-$[(en)_2Cr(OH)_2Cr(en)_2](ClO_4)_4$ were clearly different.

3. Δ,Δ-Λ,Λ-Di-*μ-hydroxobis[bis(ethylenediamine)chromium(III)] bromide*, Δ,Δ-Λ,Λ-$[(en)_2Cr(OH)_2Cr(en)_2]Br_4.4H_2O$. Δ,Δ-Λ,Λ-$[(H_2O)(en)_2Cr(OH)Cr(en)_2(OH)]Br_4.H_2O$ (2 g, 2.7 mmol) was dissolved in water (14 ml) at 30 °C. After 5 min the solution was filtered and cooled in ice for 15 min. An ice-cold mixture of equal amounts of saturated ammonium bromide and concentrated ammonia (4 ml) was added with stirring, and then solid sodium bromide (5 g) was added and cooling was continued for a further 10 min. Precipitation of the *racemic* diol bromide began within a few seconds. The precipitate was filtered off and washed twice with ice-cold water (5 ml). Drying in air yielded 1.0 g (50 %). Anal. $[(en)_2Cr(OH)_2Cr(en)_2]Br_4.4H_2O$: Cr, C, H, N, Br.

The solid salt is unstable at room temperature and a sample consisting of crystals about 1 mm in size was converted to *meso* diol within a year at this temperature. However, another sample consisting of much smaller crystals showed no isomerization within a year at room temperature.

The infrared spectra and the X-ray powder diffraction diagrams of this salt and of Δ,Λ-$[(en)_2Cr(OH)_2Cr(en)_2]Br_4.2H_2O$, respectively, were entirely different.

4. Δ,Λ-*Aqua-tetrakis(ethylenediamine)-μ-hydroxo-hydroxo dichromium(III) bromide*, Δ,Λ-$[(H_2O)(en)_2Cr(OH)Cr(en)_2(OH)]Br_4.aq$. Δ,Λ-$[(en)_2Cr(OH)_2Cr(en)_2](ClO_4)_4$ (1.5 g, 1.9 mmol) was added to 0.75 M sodium hydroxide (3 ml) and the temperature was kept at 32 °C with stirring for 15 min. Potassium bromide (0.6 g) was added and the solution was cooled to 20 °C within 5 min. The precipitated

potassium perchlorate was filtered off and to the filtered solution was added sodium bromide (2 g). After cooling to 0 °C 12 M hydrobromic acid (1 ml) was added dropwise with vigorous stirring. Ethanol (2 ml) was added and the precipitate was filtered off after 2 min. The product was immediately washed with 96 % ethanol and ether, and then stored in a vacuum desiccator at −15 °C. Yield 0.8 g (57 %). At 25 °C the solid monool bromide salt gives *meso* diol within 3 h. The X-ray powder diffraction diagram and the infrared spectrum were measured immediately after the preparation of the salt.

Conversion of racemic *isomer to* meso *isomer in solution.* Δ,Δ-Λ,Λ-$[(H_2O)(en)_2Cr(OH)Cr(en)_2(OH)]Br_4.H_2O$ (3.5 g, 4.8 mmol) was added to a 45 °C warm mixture of ethylenediamine (7.5 ml) and water (10 ml). The salt immediately dissolved and the further procedures given in preparation No. 1 were followed. This gave pure *racemic* aquahydroxo monool bromide in a yield of 1.5 g (43 %) and *meso* diol bromide in a total yield of 0.34 g (9.7 %).

Solid state reactions. Thermogravimetric measurements were made with a heating rate of 5 °C/min. The products obtained after heating have all been identified by comparing their infrared spectra with those of authentic samples. In order to make such a comparison meaningful, the heated (and dehydrated) products were reprecipitated from aqueous solution before the infrared spectra were recorded.

Potentiometric determination of the second acid dissociation constant, K_{a2}, *of the diaqua monool.* $10^{-3}-2\times10^{-3}$ M solutions of Δ,Δ-Λ,Λ-$[(H_2O)(en)_2Cr(OH)Cr(en)_2(OH)]Br_4.H_2O$ in 1.4×10^{-3} NaOH, 1 M $NaClO_4$ were made as rapidly as possible by adding the solid salt to the thermostatted base solution with vigorous stirring. The solution was kept CO_2-free by nitrogen bubbling. Reliable readings on the pH-meter could be obtained about 30 s after the time of dissolution. The measurements were continued over a period of 10 min and the pH at the time of dissolution was calculated by linear extrapolation. The definition $pH = -\log[H^+]$ was employed throughout, and concentration pH standards were made in the actual salt medium. From 6 measurements in the pH range 6.5 to 7.3 pK_{a2} was calculated (Table 2).

pH-stat measurements. The kinetics as well as the thermodynamics of the equilibrium between the monool and diol were investigated by the pH-stat technique in the pH range 6.9 to 8.6 using solutions initially prepared from diol.

1 M sodium perchlorate solutions were thermostatted (20.0 °C) and kept CO_2-free by bubbling with nitrogen before the addition of solid diol salt. The titrations were performed with 0.1000 M M NaOH, 0.9 M $NaClO_4$, and titrations were made for at least 7 half-lives of the reaction.

In no instance was the deviation between the amount of base consumed at $t=6t_{\frac{1}{2}}$ and at $t=7t_{\frac{1}{2}}$, respectively, more than 1 %, showing that equilibrium had been attained.

Spectra and kinetic runs

Spectra of monool and diol salts in different media and extrapolated to the time of dissolution (0.8 °C), as well as kinetic measurements (0.8 and 20 °C) were obtained as recently described in detail for the *meso* system.[1] The kinetic data were calculated on the basis of fixed wavelength measurements at 540 nm (0.8 °C) and at 540 and 560 nm (20 °C), and duplicate runs were always performed.

Treatment of kinetic data. All the spectrophotometric 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 %. For the spectrophotometric measurements in the $[H^+]$ region $1.0\leq[H^+]\leq10^{-4}$ M, pseudo first-order rate constants, k_{obs}, were determined from the absorbance A as function of time t, using the expression (7) by means of

$$A = a_1 + a_2\exp(-k_{obs}t) \qquad (7)$$

nonlinear regression analysis. The absorbances at $t=0$, A_o, and at equilibrium, A_∞, were then calculated from the relation $A_\infty=a_1$, and $A_o=a_1+a_2$. The calculations do not require measurements of A_∞. However, in all experiments A_∞ values were very well defined, *i.e.* A_t values at $7t_{\frac{1}{2}}$ and $8t_{\frac{1}{2}}$ were identical within experimental accuracy and deviated typically less than 1 % from calculated values of A_∞. From the potentiometric kinetic data for the $[H^+]$ region $10^{-7}\leq[H^+]\leq10^{-9}$ M, pseudo first-order rate constants, k_{obs}, were obtained graphically from the slope of plots of $\ln(B_\infty-B_t)$ against t using the relation (8), where B_t is the amount of

$$\ln(B_\infty-B_t) = \ln(B_\infty-B_o)-kt \qquad (8)$$

base consumed at time t. Infinity values, B_∞, were always well-defined and the plots were linear for at least $3t_{\frac{1}{2}}$.

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