

Thermodynamics and Kinetics for the Equilibration between Monohydroxo and Dihydroxo Bridged Binuclear Tetraammine Chromium(III) Complexes. Synthesis and Isolation of the Monohydroxo Bridged Species

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The binuclear ion $[(\text{NH}_3)_4\text{Cr}(\text{OH})_2\text{Cr}(\text{NH}_3)_4]^{4+}$ (diol) equilibrates in acid solution according to Scheme 1.

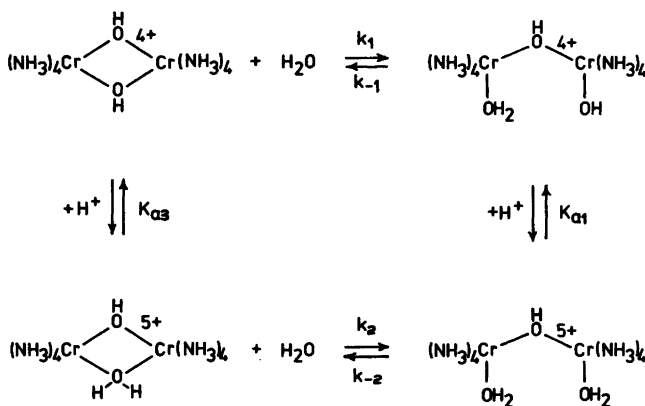
The kinetics and equilibria have been studied in 1 M $(\text{Na,H})\text{ClO}_4$ in the temperature range 25–34.4°C and the hydrogen ion concentration range 0.001–1.0 M. The results were:

$$\begin{aligned} k_1(25^\circ\text{C}) &= 1.21 \times 10^{-4} \text{ s}^{-1}; E_a = 89 \text{ kJ mol}^{-1} \\ k_{-1}(25^\circ\text{C}) &= 3.80 \times 10^{-4} \text{ s}^{-1}; E_a = 83 \text{ kJ mol}^{-1} \\ k_{-2}(25^\circ\text{C}) &= 2.7 \times 10^{-6} \text{ s}^{-1}; E_a = 126 \text{ kJ mol}^{-1} \\ k_2/K_{a3}(25^\circ\text{C}) &= 4.9 \times 10^{-5} \text{ s}^{-1} \text{ M}^{-1}; E_a(k_2) - \\ &\Delta H^\circ(K_{a3}) = 84 \text{ kJ mol}^{-1} \\ K_1(25^\circ\text{C}) &= k_1/k_{-1} = 0.318; \Delta H^\circ = +6 \text{ kJ mol}^{-1} \end{aligned}$$

The acid dissociation constants of the diaqua monool $\text{cis,cis}-[(\text{H}_2\text{O})(\text{NH}_3)_4\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_4-$

$\text{H}_2\text{O}]^{5+}$, were found to be $K_{a1}(25^\circ\text{C}) = 0.0176 \text{ M}$, $\Delta H^\circ = 49 \text{ kJ mol}^{-1}$ and $K_{a2}(25^\circ\text{C}) = 3.2 \times 10^{-8} \text{ M}$. Solid salts of both aquahydroxo monool and diaqua monool have been prepared.

It was shown recently that both isomers (Δ,Δ and Λ,Λ) of the dihydroxo bridged cation $[(\text{en})_2\text{Cr}(\text{OH})_2\text{Cr}(\text{en})_2]^{4+}$ (diol) very rapidly attain equilibrium with their corresponding monohydroxo bridged isomers $[(\text{H}_2\text{O})(\text{en})_2\text{Cr}(\text{OH})\text{Cr}(\text{en})_2(\text{OH})]^{4+}$ (monool).^{1,2} The reduced robustness of these systems is somewhat surprising when compared to the corresponding bis(tetraaqua)chromium(III) system,³ for which the rate constants are orders of magnitude smaller than those in the ethylenediamine

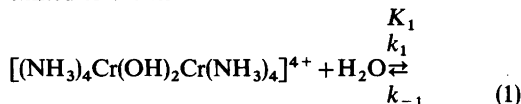


Scheme 1.

systems. The reasons for this difference are not immediately obvious, and studies on related hydroxo- and dihydroxo-bridged binuclear chromium(III) systems are clearly required for a better understanding of the factors which determine the kinetic and thermodynamic properties of such systems. We have therefore extended our previous studies on the bis(ethylenediamine)chromium(III) systems to include the tetraamminechromium(III) system, and the present work describes our results for the latter.

RESULTS

Preparations. It is now more than fifty years since Dubsy⁴ prepared salts of the dihydroxo bridged cation $[(\text{NH}_3)_4\text{Cr}(\text{OH})_2\text{Cr}(\text{NH}_3)_4]^{4+}$, diol, by heating solid *cis*- $[\text{Cr}(\text{NH}_3)_4(\text{OH})(\text{H}_2\text{O})]\text{SO}_4 \cdot \text{H}_2\text{O}$. In the present work the diol is converted to its parent monohydroxo-bridged species, monools, as follows: When $[(\text{NH}_3)_4\text{Cr}(\text{OH})_2\text{Cr}(\text{NH}_3)_4](\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$ was dissolved in 1 M HClO_4 at 55 °C the solution changed colour within minutes from purple to reddish owing to the equilibration reaction between the diol and the two monools, *i.e.* diaqua monool and aquahydroxo monool. The equilibrium between diol and aquahydroxo monool, eqn. (1), is shifted to the left.



Since the aquahydroxo monool reacts with acid giving the cation *cis,cis*- $[(\text{H}_2\text{O})(\text{NH}_3)_4\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})]^{5+}$, diaqua monool, it follows that the equilibrium is shifted toward monool in strong acid. It is important in this connection to emphasize that further acid hydrolysis of the monools, such as bridge cleavage to give the monomeric species *cis*- $[\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$, is much slower than cleavage of the first hydroxo bridge in the diol. The equilibrated acid mixture therefore contains diol and a large amount of monool, mainly as diaqua monool, and a crude tetrachlorozincate chloride salt of the latter was isolated using fractional reprecipitation (yield 79 %). From this salt a pure aquahydroxo monool salt, *cis,cis*- $[(\text{H}_2\text{O})(\text{NH}_3)_4\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_4(\text{OH})][\text{ZnCl}_3(\text{OH})](\text{ClO}_4)_2$, was prepared and from the latter a pure diaqua monool salt, *cis,cis*- $[(\text{H}_2\text{O})(\text{NH}_3)_4\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})]$

$[\text{ZnCl}_4]_2\text{Cl}$, could be obtained. The visible absorption spectra in 1.0 M HClO_4 of these two salts are identical, confirming that they are pure.

Assignment of structures. The dihydroxo bridged structure of the diol cation, $[(\text{NH}_3)_4\text{Cr}(\text{OH})_2\text{Cr}(\text{NH}_3)_4]^{4+}$, was proposed more than half a century ago by Dubsy,⁴ and has since been established by X-ray single-crystal structure analysis of the dithionate salt and the bromide salt.⁵

The monools can exist as the three isomers *cis,cis,trans,trans* and *cis,trans* where *cis* and *trans* refer to the position of H_2O or OH relative to the bridge. The proposed assignment *cis,cis* is derived from the geometry of the diol and the well-known tendency of chromium(III) mainly to undergo thermal substitution without steric change.

The hydroxo-bridged structure of the monools is supported by several observations. The acid-base properties clearly establish the presence of two terminal (nonbridging) hydroxo groups. Strong evidence for the proposed structure is also provided by the observation that an aqueous solution of the monool at $\text{pH} \approx 5$ reforms diol, which can be isolated nearly quantitatively (90 %) as the tetrachlorozincate salt. The ligand-field parameters, Δ , for the three monools are in agreement with the structure assignment. From the spectral data given in Table 1, the Δ values for the diaqua monool, the aquahydroxo monool and the dihydroxo monool, respectively, are calculated to be 19.46, 19.25 and 18.73 kK (1 kK = 1000 cm^{-1}). The observed decrease in Δ on the replacement of H_2O by OH^- is consistent with the spectrochemical series. Furthermore, the replacement of one H_2O by OH^- per Cr(III) corresponds to a decrease in Δ of 0.73 kK, and this is in excellent agreement with the corresponding decrease of 0.67 kK obtained from the Δ values⁶ of *cis*- $[\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$ and *cis*- $[\text{Cr}(\text{NH}_3)_4(\text{OH})_2]^{3+}$ ($\Delta = 20.16$ kK and 18.83 kK, respectively). Finally, it should be mentioned that the thermodynamic and kinetic results described below fully confirm the structural assignments.

The ligand-field spectra (extrapolated to the time of dissolution) of solutions of diol perchlorate salt in perchlorate medium with $[\text{H}^+]$ varying from 1.0 to 10^{-5} M were identical within experimental accuracy (Table 1), confirming the absence of a terminal non-bridging hydroxo group. This result further implies that protonation of the diol to give a μ -aqua- μ -hydroxo dimer must be negligible for solutions with $[\text{H}^+] \leq 1.0$ M. Protonation of one hydroxo bridge will certainly change the ligand

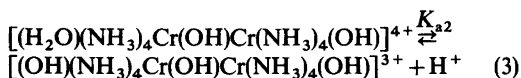
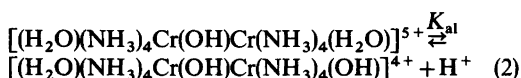
Table 1. Spectral data at 25 °C and ionic strength 1.0 M.

Cation	Medium	$(\epsilon, \lambda)_{\max}$	$(\epsilon, \lambda)_{\max}$
$[(\text{NH}_3)_4\text{Cr}(\text{OH})_2\text{Cr}(\text{NH}_3)_4]^{4+}$	1 M NaClO ₄ ^a	(124.5, 536.0)	(67.3, 386.5)
$\text{cis, cis-}[(\text{H}_2\text{O})(\text{NH}_3)_4\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})]^{4+}$	1 M(H,Na)ClO ₄ ^{b,e}	(98.0, 514.0)	(62.7, 380.0)
$\text{cis, cis-}[(\text{H}_2\text{O})(\text{NH}_3)_4\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_4(\text{OH})]^{4+}$	Pyridine buffer ^{c,e}	(97.7, 519.5)	(77.4, 385.5)
$\text{cis, cis-}[(\text{OH})(\text{NH}_3)_4\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_4(\text{OH})]^{4+}$	Ammonia buffer ^{d,e}	(100.0, 534.0)	(91.0, 402.0)

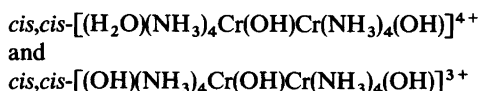
^a Measured on the perchlorate salt. Identical values were obtained in 1 M HClO₄. ^b Calculated from spectra measured in 1 M HClO₄ and in pyridine buffer. See text. ^c Buffer solutions with the composition 0.1 M pyridine, 0.76 M HClO₄, 0.24 M NaClO₄, and 0.1 M pyridine, 0.24 M HClO₄, 0.76 M NaClO₄ gave identical values. ^d Buffer solutions with the composition 0.9 M NH₃, 0.1 M NH₄ClO₄, 0.9 M NaClO₄, and 1 M NH₃, 1 M NH₄ClO₄ gave identical values. ^e All measurements made on the aquahydroxo monool salt.

field spectrum considerably, and accordingly a lower estimate for the acid dissociation constant, K_{a3} , of the μ -aqua- μ -hydroxo species of $K_{a3} \geq 30$ M can be made if it is assumed that protonation to the extent of more than 3 % would have changed the spectrum measurably.

Spectra of the diaqua monool salt (extrapolated back to the time of dissolution) were recorded at unit ionic strength, maintained constant with NaClO₄, and with $[\text{H}^+]$ varying from 1.0 M to 10^{-10} M. The absorption curves changed with $[\text{H}^+]$ and all observations were consistent with the assumption that the monools in this $[\text{H}^+]$ region attain the two acid-base equilibria, (2) and (3).



The absorption spectra for solutions of the diaqua monool salt were unchanged but different from each other in the two pH regions $4.4 \leq \text{pH} \leq 5.1$ (pyridine buffer) and $9.3 \leq \text{pH} \leq 10.2$ (ammonia buffer), respectively, and therefore represent the spectra of the cations



(Table 1). The spectrum of the diaqua monool cation, $\text{cis, cis-}[(\text{H}_2\text{O})(\text{NH}_3)_4\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})]^{5+}$, was calculated from the spectrum of the diaqua monool salt in 1 M HClO₄ and the spectrum of the aquahydroxo monool species using the value for K_{a1} determined below.

Thermodynamic measurements. The equilibrium constant for the equilibrium between monool and diol, K_1 in eqn. (1), and the first acid-dissociation constant for the diaqua monool, K_{a1} in eqn. (2), were determined simultaneously from spectrophotometric measurements. The second acid-dissociation constant for the diaqua monool, K_{a2} in eqn. (3), was determined potentiometrically.

The spectra of acidic solutions initially containing monool or diol changed with time and became constant within one to seven hours at 25 °C. The spectral changes were accompanied by well-defined isobestic points, and for each $[\text{H}^+]$ value the final spectra were identical for solutions initially containing monool and diol, respectively, as shown in Fig. 1. The final spectra clearly indicated an equi-

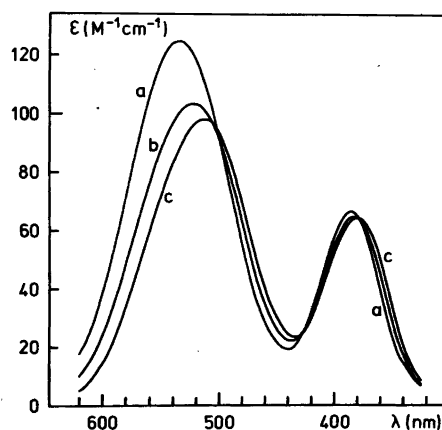


Fig. 1. Visible absorption spectra at 25 °C of 4×10^{-3} M solutions of $[(\text{NH}_3)_4\text{Cr}(\text{OH})_2\text{Cr}(\text{NH}_3)_4](\text{ClO}_4)_4$ (a) and at equilibrium (b) and of $[(\text{H}_2\text{O})(\text{NH}_3)_4\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})](\text{ZnCl}_4)_2\text{Cl}$ (c) in 0.1 M HClO₄ 0.9 M NaClO₄.

Table 2. Kinetic and thermodynamic results^a for the ammine system at ionic strength 1.0 M (Na, H)ClO₄.

Temp. °C	$k_1 \times 10^4$ s ⁻¹	$k_{-1} \times 10^4$ s ⁻¹	$k_2/K_{a3} \times 10^{5b}$ s ⁻¹ M ⁻¹	$k_{-2} \times 10^{6b}$ s ⁻¹	K_1	K_{a1} M	pK _{a2}
25.0	1.208(14)	3.80(4)	4.9(5)	2.7(3)	0.318(11)	0.0176(9)	7.50(5)
34.4	3.63(5)	10.58(15)	13.7(14)	12.7(13)	0.343(13)	0.0319(18)	—

^a Activation parameters for k_1 and k_{-1} are given in Tables 3 and 4, and ΔH° and ΔS° values for K_1 and K_{a1} are given in Table 5. ^b $\Delta H^\circ(k_2) - \Delta H^\circ(K_{a3}) = 82(11) \text{ kJ mol}^{-1}$ and $\Delta S^\circ(k_2) - \Delta S^\circ(K_{a3}) = -53(35) \text{ J mol}^{-1} \text{ K}^{-1}$. $\Delta H^\circ(k_{-2}) = 123(11) \text{ kJ mol}^{-1}$ and $\Delta S^\circ(k_{-2}) = +63(35) \text{ J mol}^{-1} \text{ K}^{-1}$.

librated solution and all observations were in agreement with the stoichiometry expressed by eqns. (1) and (2).

The spectra of the pure monool mixture and of the pure diol species, and the spectra of the equilibrium solutions were measured in the $[\text{H}^+]$ region $1.0 \geq [\text{H}^+] \geq 10^{-5} \text{ M}$. It is easily seen that all these spectra allow a determination of the equilibrium constants K_1 and K_{a1} as described in the experimental section. The results are given in Table 2.

The second acid-dissociation constant for the diaqua monool was determined by glass electrode measurements. Solutions of monool made from pure monool salts are not suitable for this purpose since both of the isolated salts contain zinc(II) whose hydroxo complex formation would seriously complicate the measurements. The problem was solved by preparing the solutions of monool *in situ* by allowing a solution of diol perchlorate (0.01 M) in 0.01 M HClO₄, 0.99 M NaClO₄ to equilibrate at 25 °C. The equilibrium solution contains 32 % monool and 68 % diol, as calculated from K_1 and K_{a1} determined above, and since the diol does not exhibit acid-base properties in this pH region, K_{a2} could be determined from pH measurements on partially neutralized solutions. However, because of a rather rapid equilibration reaction between monool and diol, a normal titration could not be performed. Each point on the titration curve had therefore to be determined using a freshly prepared equilibrated solution. pH at the time of the addition of base was then calculated by a linear extrapolation based on pH measurements within the first five to ten minutes. From four such series of measurements the value $\text{p}K_{a2} = 7.50(5)$ [25 °C, $I = 1.0 \text{ M (NaClO}_4\text{)}]$ was then calculated.

Kinetic measurements. The kinetics for the equilibrium reaction between monool and diol were investigated spectrophotometrically at two temperatures (25.0 and 34.4 °C) and at ionic strength 1.0 M

[(Na,H)ClO₄]. In all experiments pseudo first-order conditions were employed, *i.e.* the change in $[\text{H}^+]$ during the reactions was never greater than 3 %. The change of absorbancy with time followed first-order kinetics for at least $3t_{1/2}$. Pseudo first-order rate constants for the reactions initially containing monool, $k_{\text{obs}}(\text{M})$, and diol, $k_{\text{obs}}(\text{D})$, respectively, were calculated from eqn. (5) using non-linear regression analysis.

Kinetic measurements on solutions initially prepared from diol were made in the $[\text{H}^+]$ region $10^{-3} \leq [\text{H}^+] \leq 1.0 \text{ M}$. Strongly acidic solutions contain mainly monool at equilibrium (95 % monool at pH=0), and kinetic measurements on solutions initially prepared from monool cannot be accurate in this region. Measurements on solutions initially containing monool were therefore made in the $[\text{H}^+]$ region $10^{-2} \leq [\text{H}^+] \leq 0.25 \text{ M}$.

The variation of k_{obs} with $[\text{H}^+]$ is seen in Fig. 2 to be similar for the k_{obs} values obtained for solutions initially containing diol, $k_{\text{obs}}(\text{D})$, or monool, $k_{\text{obs}}(\text{M})$, and this is consistent with first-order reversible kinetics.

As established above, the stoichiometry of the equilibrium mixture can be described by the equilibrium between diol and aquahydroxo monool [eqn. (1)], and the acid-base equilibrium between the diaqua- and aquahydroxo monools [eqn. (2)]. However, the rate-expression derived from these equilibria alone is insufficient for a complete interpretation of the kinetic data, and an additional, acid-catalyzed reaction path must be included as shown in Scheme 1. From this reaction scheme the rate-expression (4) is derived:

$$\begin{aligned}
 k_{\text{calc}} &= k_{\text{calc}}(\text{D}) = k_{\text{calc}}(\text{M}) \\
 &= k_1 + \frac{[\text{H}^+]k_2}{K_{a3}} + \frac{K_{a1}k_{-1} + [\text{H}^+]k_{-2}}{K_{a1} + [\text{H}^+]} \\
 &= k_1 + \frac{[\text{H}^+]K_1k_{-2}}{K_{a1}} + \frac{K_{a1}K_1^{-1}k_1 + [\text{H}^+]k_{-2}}{K_{a1} + [\text{H}^+]} \quad (4)
 \end{aligned}$$

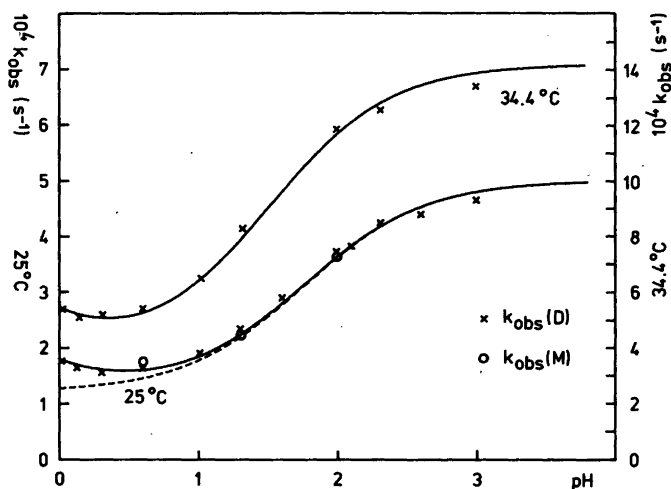


Fig. 2. The observed rate constants for the equilibration reaction between monool and diol as a function of $\text{pH} = -\log[\text{H}^+]$. The solid lines represent the calculated values of k_{obs} for the proposed acid catalyzed reaction mechanism with $K_{\text{a}1}$ and K_1 taken from Table 2. The broken line represents calculated values of k_{obs} at 25 °C, but without the acid catalyzed terms of eqn. (4), i.e. k_2 and k_{-2} have been set equal to zero.

assuming that $K_{\text{a}3} \gg [\text{H}^+]$, i.e. assuming that the protonation of the diol is stoichiometrically negligible as can be concluded from the spectral data for diol in strongly acidic media, and using the relations $K_{\text{a}3}/K_2 = K_{\text{a}1}/K_1$, $K_1 = k_1/k_{-1}$ and $K_2 = k_2/k_{-2}$.

Two of the parameters, K_1 and $K_{\text{a}1}$, in this equation have been determined thermodynamically as described above, and using these values (Table 2) our problem is then reduced to the determination of the two rate constants, k_1 and k_{-2} . This was done by the method of non-linear regression analysis

and gave the parameter values shown in Table 2. It is seen (Fig. 2) that the values of k_{calc} and k_{obs} agree excellently, and also it is noted that all parameters are well defined (Table 2). This means that the thermodynamic results are consistent with the kinetic results, thereby providing strong support for the proposed reaction mechanism.

The results also support the observation mentioned above that $K_{\text{a}3} \gg 1$, but it is not possible to determine either $K_{\text{a}3}$ or K_2 on the basis of the present data, and this is a consequence of the fact that the concentration of the μ -aqua- μ -hydroxo

Table 3. Comparison of kinetic data for the bridge-cleavage reactions of different diols. 25 °C and ionic strength 1.0 M (H, Na)ClO₄.

Diol	$k_1 \times 10^4$ s^{-1}	ΔH^\ddagger kJ mol^{-1}	ΔS^\ddagger $\text{J mol}^{-1} \text{K}^{-1}$	Ref.
$\Delta, \Delta - [(\text{en})_2\text{Cr}(\text{OH})_2\text{Co}(\text{en})_2]^{4+}$	69(9)[138(17)] ^c	78(3)	-25(12)[-20(12)] ^c	7,8 ^a
$\Delta, \Delta - [(\text{en})_2\text{Cr}(\text{OH})_2\text{Cr}(\text{en})_2]^{4+}$	69(5)	79.9(19)	-18(7)	1 ^a
$\Delta, \Delta - \Lambda, \Lambda - [(\text{en})_2\text{Cr}(\text{OH})_2\text{Cr}(\text{en})_2]^{4+}$	46.1(19)	85.0(13)	-4(5)	2 ^a
$[(\text{NH}_3)_4\text{Cr}(\text{OH})_2\text{Cr}(\text{NH}_3)_4]^{4+}$	1.21(2)	86.7(15)	-29(5)	This work
$\Delta, \Delta - \Lambda, \Lambda - [(\text{phen})_2\text{Cr}(\text{OH})_2\text{Cr}(\text{phen})_2]^{4+}$	0.69(3)	99(3)	+7(11)	9 ^b

^a Calculated from data at $t = 0.8$ and 20.0 °C in the quoted references. ^b From O¹⁸ exchange data in 0.1 M (H, Na) NO₃ and calculated from data given in the reference. ^c If it is assumed that the bridge cleavage in the mixed system essentially occurs with Cr-O bond-breaking, the k_1 value should be corrected with a statistical factor of 2 when compared with the remaining complexes giving the values in square brackets.

Table 4. Comparison of kinetic data for the reaction of aquahydroxo monool to diol. 25 °C and ionic strength 1 M (Na, H)ClO₄.^a

Aquahydroxo monool	$k_{-1} \times 10^4$ s ⁻¹	ΔH^\ddagger kJ mol ⁻¹	ΔS^\ddagger J mol ⁻¹ K ⁻¹	K_{a1} M	Ref.
$\Delta, \Delta\text{-}\Lambda, \Lambda\text{-}[(\text{H}_2\text{O})(\text{en})_2\text{Cr}(\text{OH})\text{Cr}(\text{en})_2(\text{OH})]^{4+}$	207(8)	87.2(13)	15(5)	0.29(4)	2 ^a
$\Delta, \Lambda\text{-}[(\text{H}_2\text{O})(\text{en})_2\text{Cr}(\text{OH})\text{Cr}(\text{en})_2(\text{OH})]^{4+}$	93(7)	84(2)	-0.69(7)	0.33(2)	1 ^a
$\Delta, \Lambda\text{-}[(\text{H}_2\text{O})(\text{en})_2\text{Cr}(\text{OH})\text{Co}(\text{en})_2(\text{OH})]^{4+}$	18(2)	78(3)	-37(12)	0.05(2) ^b	7,8 ^a
<i>cis, cis</i> - $[(\text{H}_2\text{O})(\text{NH}_3)_4\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_4(\text{OH})]^{4+}$	3.80(4)	80.6(15)	-40(5)	0.0176(9)	This work

^aThe parameters given here have been calculated from data at $t=0.8$ and 20.0 °C from these references (see also comments on Table 5). K_{a1} is the acid-dissociation constant of the diaquamonoools. ^bFor the mixed system K_{a1} has been measured at 0.8 °C.

species is always stoichiometrically negligible in the $[\text{H}^+]$ region used in this study. Activation parameters for the rate constants k_1 , k_{-1} and k_{-2} as well as values for the terms $\{\Delta H^\ddagger(k_2) - \Delta H^\circ(K_{a3})\}$ and $\{\Delta S^\ddagger(k_2) - \Delta S^\circ(K_{a3})\}$ are given in Tables 2, 3, and 4.

DISCUSSION

Kinetic and thermodynamic parameters for the equilibria between monoools and diol have been reported previously for the two ethylenediamine diols^{1,2} $\Delta, \Lambda\text{-}[(\text{en})_2\text{Cr}(\text{OH})_2\text{Cr}(\text{en})_2]^{4+}$ and $\Delta, \Delta\text{-}\Lambda, \Lambda\text{-}[(\text{en})_2\text{Cr}(\text{OH})_2\text{Cr}(\text{en})_2]^{4+}$, and for the heterobinuclear diol^{7,8} $(+)\text{D}\text{-}\Lambda, \Delta\text{-}[(\text{en})_2\text{Cr}(\text{OH})_2\text{Co}(\text{en})_2]^{4+}$. The ammonia system and the above-mentioned ethylenediamine systems show several common features. For each of these systems, equilibrium between the monoools and the diol is established fairly rapidly, although somewhat faster in the ethylenediamine systems than in the ammonia system. For all the complexes the equilibrium constant K_1 for the equilibrium between aquahydroxo monool and diol has a value around 1, and the diaqua monoools are all unusually acidic, having pK_{a1} values in the region 0.5–2. However, the ammonia system differs from the ethylenediamine systems by the significant acid-catalyzed contribution to the equilibration reaction between monool and diol.

The literature contains two other related but less detailed studies: Results for the 1,10-phenanthroline-diol system⁹ have been obtained from a study of the acid cleavage reaction of the diol $\Delta, \Delta\text{-}\Lambda, \Lambda\text{-}[(\text{phen})_2\text{Cr}(\text{OH})_2\text{Cr}(\text{phen})_2]^{4+}$ to give monomeric diaqua species. In the latter study the monool species was neither isolated nor characterized. However, evidence was presented that the equi-

librium constant K_1 for this system is much less than unity, and with this presumption an estimate for k_1 was obtained from O¹⁸ exchange studies.

The kinetics for the equilibrium between the aqua diol, $[(\text{H}_2\text{O})_4\text{Cr}(\text{OH})_2\text{Cr}(\text{H}_2\text{O})_4]^{4+}$, and its corresponding monool have been studied at ionic strength 2.0 and at several temperatures, and the kinetic data were interpreted in terms of a mechanism similar to that shown in Scheme 1, *i.e.*, with an acid-catalyzed and an uncatalyzed reaction path.³ The equilibrium constants, K_1 and K_{a1} , were not determined independently of the k_{obs} values, *i.e.* from A_0 and A_∞ values (although estimates for the ratio K_1/K_{a1} were obtained for ionic strengths higher than $I=2.0$). All four parameters in eqn. (4) were therefore fitted on the basis of k_{obs} data alone. However, we have made some preliminary calculations using the data for 25 °C given in Ref. 3. These calculations clearly showed that the k_{obs} data do not require the inclusion of an acid-catalyzed reaction path. Because of this ambiguity in the interpretation of the kinetic data in the aqua system, this system will not be included in the following discussion.

Comparing the pK_a values of *cis, cis*- $[(\text{H}_2\text{O})(\text{NH}_3)_4\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})]^{5+}$ with those of *cis*- $[\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$ ($pK_{a1}=4.96$ and $pK_{a2}=7.53$ in 1 M NaClO₄ at 25 °C)¹⁰, two notable differences are apparent. Firstly, the diaquamonool is a much stronger acid than the parent monomeric diaqua complex, and secondly, the difference between pK_{a1} and pK_{a2} is larger (more than two pK units) for the hydroxo-bridged system, despite the fact that the two protolytic groups are more remote in the bridged complexes.

The lower pK_{a1} value for the monool can, to some extent, be explained in terms of charge effects,

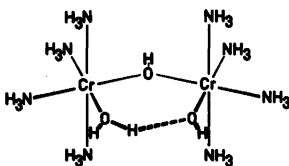


Fig. 3. The proposed hydrogen-bond stabilized structure of the aquahydroxo monool.

since we are comparing complexes with 5+ and 3+ charges, respectively. However, a charge effect alone cannot account fully for the observed difference, since on comparing the diaqua monool with the equally charged *cis*-aqua erythro ion, *cis*-[(NH₃)₅-Cr(OH)Cr(NH₃)₄(H₂O)]⁵⁺ ($pK_a = 3.5$ in 1 M NaClO₄, 25 °C),¹¹ it is seen that substitution of one water by ammonia increases pK_a by 1.5 (when comparing the acid strength of the aquaerythro with pK_{a1} for the diaqua monool, a statistical correction factor of 0.3 should be added to the latter).

As suggested previously in connection with the ethylenediamine monools,^{1,2} which exhibit the same kind of 'anomalous' acid-base properties, the increased acid strength of the diaqua monools can be explained as being due to the existence of a hydrogen bond-stabilized conformation of the corresponding bases, aquahydroxo monools, as shown in Fig. 3. A similar internal hydrogen-bond stabilization might also be operative in the diaqua- and in the dihydroxo complexes, but the very sym-

metrical conformation in the aquahydroxo complex with H₂O donating hydrogen to OH is likely to be much more stable than those of the latter. pK_a for the 4+ charged aquahydroxo monool is almost identical to that for the 2+ charged mononuclear aquahydroxo species. This is in keeping with the discussion above, since in this case the effects of charge and of hydrogen-bond stabilization work in opposite directions.

The combined effects of charge and of hydrogen-bond stabilization of the aquahydroxo monools therefore qualitatively fully account for the exceptionally small values of pK_{a1} , as well as the large difference between pK_{a1} and pK_{a2} . The values of pK_{a1} for the *meso* and *racemic* isomers of the ethylenediamine monools are almost equal but more than one pK unit less than that of the ammonia monool (Table 5). This is paralleled by a similar but significantly smaller difference in the pK_{a1} values for the parent monomeric cations: *cis*-[Cr(en)₂(H₂O)₂]³⁺ and *cis*-[Cr(NH₃)₄(H₂O)₂]³⁺ ($pK_{a1} = 4.75$ and 4.96, respectively, 25 °C, $I = 1.0$ M).¹⁰ In terms of the proposals made above, the large difference in pK_{a1} therefore could imply that in the ammonia system the hydrogen-bond stabilized conformation is less predominant than in the ethylenediamine systems, and some support for this proposal is provided by the thermodynamic parameters, ΔH° and ΔS° . The formation of the hydrogen-bond stabilized structure in Fig. 3, from the non-hydrogen-bond stabilized conformation

Table 5. Comparison of thermodynamic parameters^a for different monools and diols. 25 °C and ionic strength 1.0 M (H, Na)ClO₄.

Diol	K_1	ΔH° kJ mol ⁻¹	ΔS° J mol ⁻¹ K ⁻¹	K_{a1} M	ΔH° kJ mol ⁻¹	ΔS° J mol ⁻¹ K ⁻¹	pK_{a2}	Ref.
Δ, Λ -[(en) ₂ Cr(OH) ₂ Cr(en) ₂] ⁴⁺	0.75(2)	-3.1(9)	-13(3)	0.33(2) ^c	+12(3)	+30(9)	7.94 ^d	1 ^{b,c}
Δ, Δ - Λ, Λ -[(en) ₂ Cr(OH) ₂ Cr(en) ₂] ⁴⁺	0.22(3)	-1.9(4)	-19(13)	0.29(4)	+12(5)	+30(18)	6.87 ^e	2 ^b
[(NH ₃) ₄ Cr(OH) ₂ Cr(NH ₃) ₄] ⁴⁺	0.318(11)	+6(4)	+11(14)	0.0176(9)	+49(6)	+129(20)	7.50(5)	This work
Δ, Λ -[(en) ₂ Cr(OH) ₂ Co(en) ₂] ⁴⁺	4 ^g	-	-	0.049(17) ^d	-	-	~8 ^g	7,8
Δ, Δ - Λ, Λ -[(phen) ₂ Cr(OH) ₂ Cr(phen) ₂] ⁴⁺	≪ 1 ^f	-	-	-	-	-	-	9

^a K_1 is the equilibrium constant for the equilibrium between aquahydroxomonool and diol, and K_{a1} and K_{a2} are the acid-dissociation constants for the corresponding diaquamonools. ^b Calculated from data given at 0.8 and 20 °C in these references. The standard deviation for the equilibrium constants have been calculated from the data in these references and from the original data material of these studies. ^c For the calculations of K_{a1} the value¹⁵ $K_{a1} = 0.30$ at 20 °C has been used together with the data given in Ref. 1. ^d For $t = 0.8$ °C. ^e For $t = 20$ °C. ^f Estimated from O¹⁸ exchange data and spectrophotometric measurements in 0.1 M (Na, H)ClO₄. ^g Estimated from unpublished data.

is certainly associated with a negative ΔH° and a negative ΔS° , and in agreement with this it is observed that the greater acid strength of the ethylenediamine system is accompanied by a decrease in ΔH° which is greater than the decrease in $T\Delta S^\circ$ (Table 5).

From the data in Table 3 it is seen that the rate constant, k_1 , for the bridge cleavage reaction of the different diols decreases in the order Δ, Λ -en > Δ, Δ - Λ, Λ -en > NH_3 > 1,10-phen, and this order is followed by an increase in ΔH^\ddagger . This relationship between k_1 and ΔH^\ddagger is normal for series of reactions of chromium(III) reactions.

The data given in Table 3 for the mixed diol, Δ, Λ - $[(\text{en})_2\text{Cr}(\text{OH})_2\text{Co}(\text{en})_2]^{4+}$, place this complex in the above sequence close to the *meso* ethylenediamine diol, both with respect to k_1 and ΔH^\ddagger , which might suggest that in the mixed diol the k_1 path is essentially associated with Cr-O bond cleavage.

In the following discussion concerning the reaction of aquahydroxo monool to give diol, with rate constant k_{-1} , the data for the mixed CrCo system are included even though k_{-1} for the mixed system is a composite term due to the fact that ring-closure can occur both *via* Cr-OH₂ and Co-OH₂ bond-breaking. K_{a1} for the mixed system is also a composite term since deprotonation to form aquahydroxo monool can occur at two different metal centres. The following discussion should therefore be read with these reservations in mind. However, since bridge cleavage in the mixed diol probably occurs by Cr-O bond cleavage as suggested above, it seems probable, following the principle of microscopic reversibility, that k_{-1} is essentially associated with Cr-OH₂ bond-breaking.

From the data in Table 4 it is seen that the rate constant for diol formation, k_{-1} , for the ammonia monool and the three ethylenediamine monools decreases in the order Δ, Δ - Λ, Λ -CrCr > Δ, Λ -CrCr > Δ, Λ -CrCo > NH_3 -CrCr. This order is at the same time the order of decreasing acid strength, K_{a1} , of the corresponding monools, and therefore, following the discussion above, it is the order of decreasing internal hydrogen-bond stabilization of the aquahydroxo monools. In order to explain this apparent correlation between k_{-1} and K_{a1} , we consider the possible effect on k_{-1} of the formation of hydrogen-bond stabilized conformations of the aquahydroxo monools.

Firstly, it is clearly reasonable to assume that the hydrogen-bond stabilized conformation resembles

the transition state more than other conformations and should therefore contribute to k_{-1} by an enhancement of ΔS^\ddagger . Simultaneously, the internal hydrogen bond has to be broken and this bond-breaking will contribute to k_{-1} in terms of increasing ΔH^\ddagger . We therefore expect increasing ΔS^\ddagger to be associated with increasing ΔH^\ddagger and this is in good agreement with the experimental result of Table 4.

From the above discussion it is not possible to predict any relationship between k_{-1} and the degree of hydrogen-bond stabilization. The observation that increasing k_{-1} values are associated with increasing ΔS^\ddagger values is in the present case seen to be caused by a larger increase in $T\Delta S^\ddagger$. We therefore conclude that an increased hydrogen-bond stabilization of the aquahydroxo monool may be responsible for a simultaneous increase of K_{a1} and of the activation parameters ΔH^\ddagger and ΔS^\ddagger for the monool \rightarrow diol reaction.

The equilibration reaction between monool and diol in the ammonia system proceeds *via* two reaction paths, the uncatalyzed reaction path (k_1 and k_{-1}) discussed above and an acid-catalyzed path (k_2/K_{a3} and k_{-2}) involving protonation of the diol hydroxo bridge. The acid-catalyzed contribution to k_{obs} is significant at low pH as shown in Fig. 2 and is $\sim 30\%$ at pH=0 (25 °C). A corresponding acid-catalysis term was not found in the ethylenediamine systems or the phenanthroline system and, as discussed before, the occurrence of an acid-catalyzed reaction path in the aqua system is not clearly established.

The rate of the reaction of the diaqua monool to give the aqua-bridged intermediate (k_{-2}) is ~ 100 times smaller than that of the aquahydroxo monool to give diol. This is not surprising since coordinated water is certainly a poorer nucleophile than coordinated hydroxide. Both reactions involve displacement of coordinated water but the activation parameters, ΔH^\ddagger , are significantly different. This suggests an associative mechanism for both the k_{-1} and k_{-2} pathways, since in terms of an essentially dissociative mechanism the rate of chromium-water bond-breaking to form the transition state would probably be rather similar for the two monools and should thus lead to similar ΔH^\ddagger values.

An associative mechanism is clearly in keeping with the discussion above in connection with k_{-1} , and it is also in agreement with the well-documented fact that the water-exchange reactions of chromium(III) amines, $[\text{Cr}(\text{NH}_3)_{6-n}(\text{H}_2\text{O})_n]^{3+}$, are essentially associative.^{12,13} The rate constant

for exchange of one water in $cis\text{-}[\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$ is $5.9 \times 10^{-5} \text{ s}^{-1}$ at 25°C ($I=1.0 \text{ M}$), and the activation parameters are $\Delta H^\ddagger = 95.0 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -7(6) \text{ J mol}^{-1} \text{ K}^{-1}$.¹⁴ Comparing these values with those for k_{-2} , it is seen that the nucleophilicity of water is tremendously decreased on coordination, reflected by a very large ΔH^\ddagger (k_{-2}) value. However, despite this, k_{-2} is only a factor of 20 less than the rate of water exchange, and this is due to a proximity effect, *i.e.* a very large ΔS^\ddagger (k_{-2}) value.

EXPERIMENTAL

Materials. The complex $[(\text{NH}_3)_4\text{Cr}(\text{OH})_2\text{Cr}(\text{NH}_3)_4](\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$ was prepared as described in the literature.⁶ All 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 spectrophotometric measurements in the visible region. For the spectrophotometric data given above the molar absorptivity ϵ is given in $\text{l mol}^{-1} \text{ cm}^{-1}$ and the wavelength λ in nm. The molarity of solutions of the binuclear complexes is in all cases defined in terms of the number of mol of complex, rather than the number of mol of chromium(III), per litre of solution.

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.

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

Preparations. 1. μ -Hydroxo- $[cis\text{-tetraammineaquachromium(III)}]$ ($cis\text{-tetraamminehydroxochromium(III)}$) trichlorohydroxozincate diperchlorate, $cis,cis\text{-}[(\text{H}_2\text{O})(\text{NH}_3)_4\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_4(\text{OH})][\text{ZnCl}_3(\text{OH})](\text{ClO}_4)_2$. Solid $[(\text{NH}_3)_4\text{Cr}(\text{OH})_2\text{Cr}(\text{NH}_3)_4](\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$ (20.0 g, 28.2 mmol) was added to hot (55°C) 1 M HClO_4 (120 ml). The diol salt dissolved within one minute and the colour changed from purple to reddish within minutes. The solution was kept at 55°C for 15 min and to the resulting red solution was then added a saturated solution of NaClO_4 (35 ml) with stirring and cooling

in ice for about $\frac{1}{2}$ hour. The resulting precipitate of unreacted diol perchlorate salt (2.0 g) was filtered off. Addition of an ice-cold mixture of 12 M HCl (20 ml) and 4 M Li_2ZnCl_4 (40 ml) to the cold filtrate caused almost instantaneous precipitation of a crude diaqua monool salt,

$cis,cis\text{-}[(\text{H}_2\text{O})(\text{NH}_3)_4\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})][\text{ZnCl}_4]_2\text{Cl}$, which was contaminated with a small amount of diol salt. The precipitate was filtered off, washed thoroughly with 96% ethanol and dried in the air (yield 16.5 g, 79%). This crude product (16.5 g) was dissolved in water (140 ml) at 0°C and ice-cold 6 M LiCl (35 ml) and then a saturated (20°C) solution of sodium perchlorate (35 ml) were added with cooling in an ice-bath and stirring. After 15 min a very small amount of purple diol salt was filtered off. 2 M sodium acetate (35 ml) was then added to the filtrate with continued stirring and cooling in ice, and red crystals precipitated almost immediately. The precipitate was isolated as above. The yield was 11.9 g (62%) of a pure salt.

Anal. $[(\text{H}_2\text{O})(\text{NH}_3)_4\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_4(\text{OH})][\text{ZnCl}_3(\text{OH})](\text{ClO}_4)_2$: Cr, H, N, Zn, Cl (ionic) and Cl (covalent). The salt is light-sensitive and was therefore stored in the dark. Visible absorption spectra are given in Table 1. The salt is soluble in water and in strong acids such as hydrochloric acid and perchloric acid.

2. μ -Hydroxo-bis($cis\text{-tetraammineaquachromium(III)}$) ditetrachlorozincate chloride, $cis,cis\text{-}[(\text{H}_2\text{O})(\text{NH}_3)_4\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})][\text{ZnCl}_4]_2\text{Cl}$. Pure $cis,cis\text{-}[(\text{H}_2\text{O})(\text{NH}_3)_4\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_4(\text{OH})][\text{ZnCl}_3(\text{OH})](\text{ClO}_4)_2$ (5.0 g, 7.35 mmol) was dissolved at 0°C in 1 M HCl (100 ml) and to the stirred solution was then added 4 M Li_2ZnCl_4 (25 ml) with cooling in ice. Red crystals of the diaqua monool precipitated almost immediately. The precipitate was filtered off and washed with 96% ethanol and dried in the air. The yield was 5.3 g (97%) of a pure salt. Anal. $[(\text{H}_2\text{O})(\text{NH}_3)_4\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})](\text{ZnCl}_4)_2\text{Cl}$: Cr, H, N, Zn, and Cl.

Potentiometric determination of the second acid-dissociation constant K_{a2} of the diaquamonool. A $1.00 \times 10^{-2} \text{ M}$ solution of $[(\text{NH}_3)_4\text{Cr}(\text{OH})_2\text{Cr}(\text{NH}_3)_4](\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$ in 10^{-2} M HClO_4 , 0.99 M NaClO_4 was kept at 25°C for 3 h. This gave an equilibrated solution containing 67.6% diol and 32.4% monool as calculated from the values of K_{a1} and K_1 given in Table 2. Aliquots of this equilibrium solution were then added to the appropriate volume of thermostatted 10^{-2} M NaOH , 0.99 M NaClO_4 with vigorous stirring.

Reliable readings on the pH-meter could be obtained about 30 s after the time of mixing. The measurements were continued over a period of 10 min and the pH at the time of mixing was determined by linear extrapolations which typically showed $\Delta \text{pH}/\Delta \text{min} \approx 0.02$. The definition $\text{pH} =$

$-\log[H^+]$ was employed throughout, and concentration pH standards were made in the actual salt medium. pK_{a2} was calculated from 5 such series of measurements in the pH range of 7.0 to 7.9 (Table 2).

Spectra and treatment of spectral data. Spectra of monool and diol salts in the various media were obtained as recently described in detail for the *meso* ethylenediamine system.¹

Kinetic measurements were made under pseudo first-order conditions, *i.e.* the change in hydrogen-ion concentration during a kinetic run never exceeded 3%. Pseudo first-order rate constants, k_{obs} , were calculated from the absorbance A as function of time t by means of non-linear regression analysis, using the expression (5) where A_0 is the

$$A = A_\infty + (A_0 - A_\infty) \exp(-k_{obs}t) \quad (5)$$

absorbance at $t=0$ and A_∞ is the absorbance at equilibrium. The rate constants were calculated on the basis of absorbances measured at wavelengths 560 and 540 nm, and duplicate kinetic runs were always made. The activation parameters ΔH^\ddagger and ΔS^\ddagger were calculated from eqn. (6),

$$k_r = (kT/h) \exp(-\Delta H^\ddagger/RT + \Delta S^\ddagger/R) \quad (6)$$

The equilibrium constants K_{a1} and K_1 were calculated from ϵ_0 and ϵ_∞ values obtained for solutions initially containing diol [$\epsilon_0(D)$ and $\epsilon_\infty(D)$] or monool [$\epsilon_0(M)$ and $\epsilon_\infty(M)$], the ϵ -values being measured at the four wavelengths 560, 540, 400 and 380 nm. At 560 and 540 nm, ϵ_0 and ϵ_∞ values were calculated using A_0 and A_∞ values from the kinetic calculation [eqn. (5)]. At 400 and 380 nm A_0 values were obtained by linear extrapolation back to the time of dissolution and A_∞ values were measured at $t=7t_{1/2}$. The variation in the observed ϵ -values with the hydrogen-ion concentration, at a given wavelength and temperature, can be expressed by eqns. (7)–(9), where ϵ_1 , ϵ_2 and ϵ_3 are the

$$\epsilon_0(D) = \epsilon_1 \quad (7)$$

$$\epsilon_0(M) = \frac{\epsilon_2 \cdot K_{a1} + \epsilon_3 [H^+]}{K_{a1} + [H^+]} \quad (8)$$

$$\begin{aligned} \epsilon_\infty(M) = \epsilon_\infty(D) = \\ \frac{\epsilon_1 K_{a1} + \epsilon_2 K_{a1} K_1 + \epsilon_3 [H^+] K_1}{K_{a1} + K_{a1} K_1 + [H^+] K_1} \end{aligned} \quad (9)$$

molar absorption coefficients of diol, aquahydroxo monool and diaqua monool, respectively. These parameters together with K_{a1} and K_1 were then fitted using least-square non-linear regression analysis. The calculations were made simultaneously for data obtained at the two temperatures 25.0 and

34.4°C. Data for ϵ_0 and ϵ_∞ were obtained for solutions with $[HClO_4]$ varying from 1 to 10^{-3} M. In some experiments the actual concentration of hydrogen ion deviated from the stoichiometric concentration of perchloric acid due to the acid-base equilibrium [eqn. (2)]. These deviations were never greater than 3% and were accounted for in the final calculations.

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