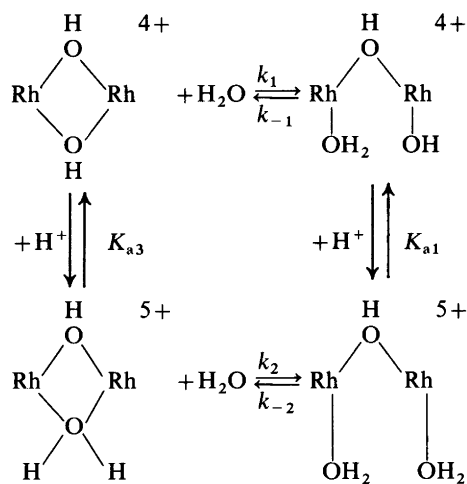


Equilibria between Monohydroxo and Dihydroxo-bridged Binuclear Ethylenediamine Rhodium(III) Complexes

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The binuclear ion Δ, Λ - $[(en)_2Rh(OH)_2Rh(en)_2]^{4+}$ (diol) equilibrates in acid solution according to Scheme 1 (amine ligands omitted).



Scheme 1.

The kinetics and equilibria have been studied in 1 M (Na,H)ClO₄ in the temperature range 25–40 °C and the hydrogen ion concentration range 10⁻⁵–0.1 M. The results were:

$$\begin{aligned}
 k_1 (25^\circ\text{C}) &= 4.6(1) \times 10^{-4} \text{ s}^{-1}; \\
 \Delta H^\ddagger &= 86(3) \text{ kJ mol}^{-1}. \\
 k_{-1} (25^\circ\text{C}) &= 4.1(1) \times 10^{-5} \text{ s}^{-1}; \\
 \Delta H^\ddagger &= 101(3) \text{ kJ mol}^{-1}. \\
 k_{-2} (25^\circ\text{C}) &= 5.1(1) \times 10^{-5} \text{ s}^{-1}; \\
 \Delta H^\ddagger &= 100(2) \text{ kJ mol}^{-1}. \\
 k_2/K_{a3} (25^\circ\text{C}) &= 0.134(3) \text{ s}^{-1} \text{ M}^{-1}; \\
 \Delta H^\ddagger(k_2) - \Delta H^\circ(K_{a3}) &= 58(2) \text{ kJ mol}^{-1}. \\
 K_1 (25^\circ\text{C}) &= k_1/k_{-1} = 11.2(5); \\
 \Delta H^\circ &= -14(3) \text{ kJ/mol}^{-1}.
 \end{aligned}$$

The acid dissociation constants for the diaqua monool, Δ, Λ - $[(\text{H}_2\text{O})(en)_2Rh(\text{OH})Rh(en)_2(\text{H}_2\text{O})]^{5+}$, were found to be $pK_{a1} (25^\circ\text{C}) = 2.372(7)$ ($\Delta H^\circ = 28(4) \text{ kJ mol}^{-1}$ and $\Delta S^\circ = 49(13) \text{ J mol}^{-1} \text{ K}^{-1}$) $pK_{a2} (25^\circ\text{C}) = 9.128(7)$.

Additional kinetic data at ionic strength 0.1 M and at 25 °C support the proposed mechanism. From kinetic data in the basic pH region it was established that base catalysis is unimportant for $\text{pH} \leq 9.5$. At higher pH base catalysis does occur, and in 0.01 M NaOH 0.99 M NaClO₄ cleavage of diol to dihydroxo monool is fast, $k_{\text{obs}} (25^\circ\text{C}) = 2.10(2) \times 10^{-3} \text{ s}^{-1}$.

The aquahydroxo monool was isolated as a solid salt, Δ, Λ - $[(\text{H}_2\text{O})(en)_2Rh(\text{OH})Rh(en)_2(\text{OH})]-(\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$.

A revised synthesis for the preparation of *cis*- $[\text{Rh}(\text{en})_2(\text{OH})(\text{H}_2\text{O})]\text{S}_2\text{O}_6$ is given and the acid dissociation constants for *cis*- $[\text{Rh}(\text{en})_2(\text{H}_2\text{O})_2]^{3+}$ were determined to be $pK_{a1} (25^\circ\text{C}) = 6.338(2)$ and $pK_{a2} (25^\circ\text{C}) = 8.244(2)$ in 1 M NaClO₄.

A considerable amount of work has been done on the kinetics and thermodynamics of the bridge cleavage reactions of polynuclear hydroxo-bridged complexes of Co(III) and Cr(III) in aqueous solution.^{1–19} In our own laboratory attention has centered on the so-called ‘diol’ complexes of Cr(III), *i.e.* binuclear dihydroxo-bridged species of the type $[(en)_2\text{Cr}(\text{OH})_2\text{Co}(\text{en})_2]^{4+}$ and $[\text{L}_4\text{Cr}(\text{OH})_2\text{CrL}_4]^{4+}$ ($\text{L} = \text{NH}_3, \frac{1}{2}\text{en}$), for which the kinetics and thermodynamics of the hydroxo bridge cleavage reaction in acidic solution to give monohydroxo-bridged species, ‘monool’, have been investigated in detail.^{14–19}

In these systems the monool species have been isolated as crystalline salts and are well-char-

acterized,²⁰ and studies of the equilibration between monool and diol can be made without complications due to loss of ammine or amine ligands or further hydrolysis to give monomeric complexes. In the case of Co(III) diols, in none of the systems examined have the monool species been isolated or characterized definitively, so that an unequivocal interpretation of the kinetic data is not possible.^{3,4}

Very little is known about the corresponding Rh(III) reactions.²¹ Following the synthesis²² of the rhodium(III) diols with ammonia and ethylenediamine it was, therefore, natural to extend the previous investigations to include the latter complexes, and the present work describes our results for the Rh(III) ethylenediamine system. Work on the Rh(III) ammonia system is in progress and will be reported later.

RESULTS

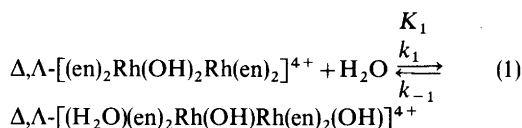
Synthesis and properties of the complexes. The rhodium diol was synthesized recently from *cis*-[Rh(en)₂(OH)(H₂O)]S₂O₆, which on heating to 120 °C for 24 h gives Δ,Λ-[en)₂Rh(OH)₂Rh(en)₂](S₂O₆)₂ quantitatively.²² This salt, which is rather insoluble in water, is converted to the more soluble bromide salt by treatment with ammonium bromide and purified by reprecipitation. However, with the latter procedure there exists the possibility of contamination of the sample with monohydroxo-bridged species, monools, formed by the fairly rapid equilibration reaction between diol and monool (*vide infra*). In order to avoid this complication the reprecipitation of the diol bromide salt has to be carried out as quickly as possible and in the cold, as described in a modified procedure given in this work. The diol perchlorate salt which has been used in the present study was obtained from the bromide salt using standard procedures.²³

A slightly revised procedure for the synthesis of *cis*-[Rh(en)₂(OH)(H₂O)]S₂O₆ and a procedure for reprecipitation of this salt is given. In this connection it should be mentioned that the *cis*-dichloro complex, which is used for the synthesis of the *cis*-aqua-hydroxo salt, was previously²⁴ formulated incorrectly as a chloride salt and that the correct formulation is *cis*-[Rh(en)₂Cl₂](Cl)₃(ClO₄)₄.

The acid dissociation constants for *cis*-[Rh(en)₂(H₂O)₂]³⁺ were determined by glass-electrode measurements using *cis*-[Rh(en)₂(OH)(H₂O)]S₂O₆ and the values pK_{a1} = 6.338(2) and pK_{a2} = 8.244(2)

were obtained for unit ionic strength (NaClO₄) at 25 °C. These values are close to those previously²⁵ reported for ionic strength 0.5 M (6.09 and 8.08) and for ionic strength 0.01 M (5.82 and 7.98) at 25 °C.

In the following the synthesis of a monohydroxo-bridged species from diol is described. The diol is very robust in acid solution with respect to hydrolysis of the amine ligands, but cleavage of one hydroxo bridge occurs fairly rapidly as can be seen in eqn. (1).

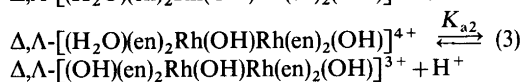
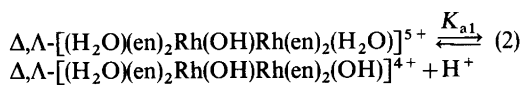


Further acid hydrolysis of the monools, such as bridge cleavage to give the monomeric species, *cis*-[Rh(en)₂(H₂O)₂]³⁺, is much slower. The equilibrium above lies very much to the right, and when a suspension of Δ,Λ-[en)₂Rh(OH)₂Rh(en)₂](ClO₄)₄ in water is heated to 55 °C for a few minutes the resulting solution contains essentially aquahydroxo monool, which can be precipitated as its perchlorate salt, Δ,Λ-[(H₂O)(en)₂Rh(OH)Rh(en)₂(OH)](ClO₄)₄ · H₂O. This crude product, which is slightly contaminated with diol, is then dissolved in 1 M perchloric acid, whereupon the aquahydroxo salt is converted completely into the much more soluble diaqua salt. Under the acidic conditions the small residual amount of diol is rapidly hydrolyzed to monool, and the resulting solution contains pure diaquamonool. From the data presented later in this work it can easily be calculated that an equilibrium solution with [H⁺] = 1.0 M (25 °C) contains 99.5 % monool. Subsequent addition of the appropriate amount of base leads to precipitation of pure Δ,Λ-[(H₂O)(en)₂Rh(OH)Rh(en)₂(OH)](ClO₄)₄ · H₂O. The purity of this compound, which is very crucial for the accuracy of the spectrophotometric determination of the equilibrium constant K₁ in eqn. (1) (*vide supra*), was checked by observing that the absorption spectrum measured in 1 M NaClO₄ (for the entire region 350–240 nm) did not change upon further reprecipitations.

Solid Δ,Λ-[(H₂O)(en)₂Rh(OH)Rh(en)₂(OH)](ClO₄)₄ · H₂O is stable at room temperature for days, but at elevated temperatures it is converted into diol. For example, heating of solid monool salt for two hours at 100 °C resulted in almost quantitative conversion into diol.

The absorption spectra of aqueous solutions of Δ, Λ -[(en)₂Rh(OH)₂Rh(en)₂](ClO₄)₄ changed with time due to the monool-diol equilibration reaction, and linear extrapolation back to the time of dissolution had therefore to be made. Such extrapolations can be made linearly only if based on measurements taken within a period after the time of dissolution which is short relative to the time-scale of the equilibration reaction. This could be done at 25 °C for weakly acidic solutions where the equilibration takes hours. In strongly acidic solutions the reaction is very fast, and additional measurements have therefore been made at 0 °C. The observation that identical spectra have been obtained for [H⁺] varying from 0.1 M to ~10⁻¹² M (Table 1) confirms the absence of a terminal non-bridging hydroxo group. The result further implies that protonation of the diol to give μ -aqua- μ -hydroxo species must be negligible for solutions with [H⁺] ≤ 0.1 M. The observation that the spectrum is unchanged even in 0.01 M NaOH, 0.99 M NaClO₄ implies that the acid-base equilibrium between diol and an oxo-bridged species must have pK_a ≥ 14.

Spectra of the monool salt were measured in the entire [H⁺] region 1.0 ≥ [H⁺] ≥ 10⁻¹³ M. All the spectral measurements could be interpreted in terms of the two consecutive acid-base equilibria given in eqns. (2) and (3).



Spectral data for the three monool cations are presented in Table 1. The result further shows that deprotonation of the hydroxo bridge to form an oxo-bridged species is unimportant for pH ≤ 13.

The proposed hydroxo-bridged structure of the monool species follows from the acid-base properties, which clearly establish the presence of two terminal (non-bridging) hydroxo groups (*vide infra*). Strong evidence for the proposed structure is also provided by the observation that solid Δ, Λ -[(H₂O)(en)₂Rh(OH)Rh(en)₂(OH)](ClO₄)₄ · H₂O readily forms diol on heating. The structure assignment is also in agreement with the thermodynamic and kinetic results discussed below. The assignment of the configuration as Δ, Λ is based on the configura-

Table 1. Ligand-field spectra extrapolated to the time of dissolution at 25 °C.

Compound	Medium ^a	(ϵ, λ) _{max}	(ϵ, λ) _{max}	(ϵ, λ) _{min}
Δ, Λ -[(en) ₂ Rh(OH) ₂ Rh(en) ₂](ClO ₄) ₄	0.125 M HClO ₄ ^b	(532,331)	(532,331)	(370,301)
	0.001 M HClO ₄	(535,331)	(535,331)	(375,301)
	Buffer pH = 9.5 ^c	(528,331)	(528,331)	(367,301)
	0.01 M NaOH	(531,331)	(531,331)	(377,301)
Δ, Λ -[(en) ₂ Rh(OH) ₂ Rh(en) ₂]Br ₄ · 2H ₂ O	0.001 M HClO ₄	(526,331)	(526,331)	(368,301)
	1 M HClO ₄	(590,329)	(590,329)	(445,299)
	0.1 M HClO ₄	(597,329)	(597,329)	(448,299)
	0.05 M NaOH	(519,327)	(519,327)	(487,309)
Δ, Λ -[(H ₂ O)(en) ₂ Rh(OH)Rh(en) ₂ (OH)](ClO ₄) ₄ · H ₂ O	Buffer pH = 10.5 ^c	(520,327)	(520,327)	(488,309)
	1 M NaClO ₄	(514,330)	(514,330)	(391,302)
	Buffer pH = 5.2 ^d	(516,330)	(516,330)	(391,302)
			(553,273) (559,273) (635,278) (638,278) (553,270) ^{sh} — ^e	(445,299) (448,299) (487,309) (488,309) (391,302) (391,302)

^a Unit ionic strength maintained with NaClO₄. The concentration of complex was always ~10⁻³ M. ^b Measured at 0.8 °C. ^c 0.01 M NH₄ClO₄, 0.01 M NH₃, 0.99 M NaClO₄ (pH = 9.5) and 0.01 M NH₄ClO₄, 0.1 M NH₃, 0.99 M NaClO₄ (pH = 10.5). ^d 0.1 M py, 0.9 M NaClO₄ (py = pyridine). ^e Obscured by absorption band of pyridine.

Table 2. Thermodynamic data for monools and diol at 25 °C and unit ionic strength, (Na,H)ClO₄.^a

pK-values	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ deg ⁻¹)
pK _{a1}	2.372(7)	28(4)
pK _{a2}	9.128(7)	—
K ₁	11.2(5)	-14(3)
		-28(8)

^a K₁, K_{a1} and K_{a2} are defined by eqns. (1), (2) and (3), respectively.

tion of the parent diol and the well-known tendency of Rh(III) to undergo substitution reactions without isomerization.

Determination of the acid dissociation constants for the monools. The two acid dissociation constants K_{a1} and K_{a2} for the diaqua monool were determined by glass-electrode measurements. Owing to the equilibration reaction between the monool and diol a normal titration could not be made. Each pH measurement was therefore made on a freshly prepared solution, and pH was then extrapolated back to the time of dissolution. At higher temperatures this method becomes difficult since equilibration is then fast relative to the response of the glass electrode. The determination of pK_{a1} at 35.0 °C was therefore made using equilibrium conditions (see experimental section). The results are quoted in Table 2.

Measurement of the kinetics and thermodynamics of the equilibrium between monool and diol. The kinetics and thermodynamics of the equilibrium between monool and diol were studied spectrophotometrically in the [H⁺] region 0.1 ≥ [H⁺] ≥ 10⁻⁵ M. The rate of equilibration is very pH-dependent, as is also that of the subsequent

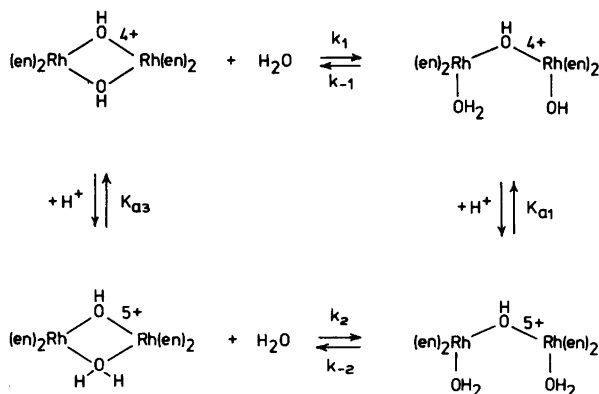
hydrolysis of the monools to monomeric *cis*-[Rh(en)₂(H₂O)₂]³⁺. However, at a given [H⁺] the latter reaction is always much slower, by a factor of at least 100, than the former reaction.

The spectra of solutions initially containing diol and monool, respectively, changed with time and became constant within a period varying from minutes to hours at 25 °C, depending on pH. The spectral changes were always attended by well-defined isosbestic points, and for a given [H⁺] the final spectra were identical for solutions initially containing monool and diol, respectively. The final spectra are thus those of equilibrium mixtures of monool (diaqua and aquahydroxo) and diol, and the stoichiometry of the solutions can therefore be expressed by eqns. (1), (2) and (3).

The equilibrium constant K₁ was determined spectrophotometrically from measurements in solutions with [HClO₄] = 10⁻³, 5 × 10⁻⁴ and 10⁻⁴ M, respectively (see also experimental section). From measurements at the two temperatures 25.0 and 40.6 °C the parameters quoted in Table 2 were calculated.

Kinetic data were obtained from spectrophotometric measurements, and pseudo first-order rate constants, k_{obs}, for solutions initially containing pure diol or pure monool were calculated using non-linear regression analysis. Most of the kinetic measurements were made on solutions initially containing diol, and [H⁺] was varied from 0.1 to 10⁻⁵ M.

Kinetic measurements on solutions initially containing monool were made only for [H⁺] = 10⁻³ and 10⁻⁴ M. At higher [H⁺] and in the basic region there is practically no change of absorbance with time for solutions initially containing monool.



Scheme 2.

All kinetic measurements were made under pseudo first-order conditions, *i.e.* the change in the hydrogen-ion concentration during an experiment was typically less than 3 %.

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 monoools [eqn. (2)]. However, the rate-expression derived from these equilibria alone is insufficient for an interpretation of the kinetic data and an additional, acid-catalyzed reaction path must be included as shown in Scheme 2. From this reaction scheme the following rate-expression is derived assuming that $K_{a3} \geq [H^+]$, *i.e.* that 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 $K_{a3}/K_2 = K_{a1}/K_1$, $K_1 = k_1/k_{-1}$ and $K_2 = k_2/k_{-2}$; eqn. (4). Two of the parameters, K_1

$$k_{\text{calc}} = k_1 + \frac{[H^+]K_1k_{-2}}{K_{a1}} + \frac{K_{a1}K_1^{-1}k_1 + [H^+]k_{-2}}{K_{a1} + [H^+]} \quad (4)$$

and K_{a1} , in this equation have been determined in separate experiments as described above. Using these values, the two rate constants, k_1 and k_{-2} , were determined by the method of non-linear regression analysis (Fig. 1) and gave the parameter values shown in Table 3.

Additional kinetic measurements made at ionic strength 0.1 M (Na,H)ClO₄ and 25 °C showed a linear relationship between k_{obs} and $[H^+]$. From the calculations above it is seen that this linear

Table 3. Kinetic data for the equilibration reactions between monoools and diol at 25 °C and ionic strength 1.0 M (Na,H)ClO₄.

Reaction	$10^5 \times k$ s ⁻¹	ΔH^\ddagger kJ mol ⁻¹	ΔS^\ddagger J mol ⁻¹ deg ⁻¹
k_1	45.6(11)	86(3)	-19(8)
k_{-1}	4.07(10)	101(3)	9(9)
k_{-2}	5.10(12)	100(2)	9(7)
Reaction	k s ⁻¹ M ⁻¹	$\Delta H^\ddagger - \Delta H^\circ$ kJ mol ⁻¹	$\Delta S^\ddagger - \Delta S^\circ$ J mol ⁻¹ deg ⁻¹
k_2/K_{a3}	0.134(3)	57.8(20)	-68(7)

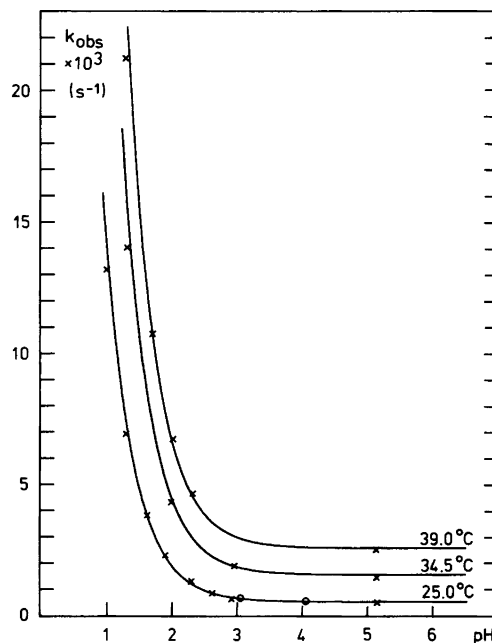


Fig. 1. The observed pseudo first-order rate constants, k_{obs} , for the equilibration reaction between monool and diol as a function of $\text{pH} = \log[H^+]$ at three different temperatures and at unit ionic strength. The k_{obs} values have been obtained for solutions initially containing diol (x) or monool (o). The solid lines represent calculated values of k_{obs} [eqn. (4)] with parameters as quoted in Tables 2 and 3.

relationship is accidental and is due to the fact that the values of k_{-1} and k_{-2} are almost equal. This reduces eqn. (4) to the approximate relationship (5). Assuming that this approximate equa-

$$k_{\text{calc}} = k_1 + k_{-1} + \frac{[H^+]k_2}{K_{a3}} \quad (5)$$

tion can be applied to the data for $I=0.1$ M, the values $k_2/K_{a3} = 5.2(1) \times 10^{-2} \text{ s}^{-1} \text{ M}^{-1}$ and $k_1 + k_{-1} = 4.83(10) \times 10^{-4} \text{ s}^{-1}$ were then calculated (Table 4). Since K_1 and K_{a1} were not determined at $I=0.1$ M, any further interpretation of the kinetic data was not possible.

A few kinetic measurements were made in the basic region (at 25 °C and ionic strength 1.0 M). At $\text{pH} = 9.5$ (0.01 M NH₃, 0.01 M NH₄ClO₄, 0.99 M NaClO₄), the value for k_{obs} of $4.68(10) \times 10^{-4} \text{ s}^{-1}$ is in good agreement with the value $4.57(11) \times$

Table 4. Observed and calculated rate constants for the equilibrium between the monools and the diol at ionic strength 0.1 M (Na,H)ClO₄ and at 25 °C. k_{calc} from eqn. (5).

[H ⁺] mol/l	$10^4 \times k_{\text{obs}}$ s ⁻¹	$10^4 \times k_{\text{calc}}$ s ⁻¹
0.1	55.8	56.8
0.05	31.0	30.8
0.01	10.3	10.0
0.002	5.92	5.87
5×10^{-6} ^a	4.77	4.83

^a0.01 M pyH₂ClO₄, 0.01 M py, 0.09 M NaClO₄ (py = pyridine).³⁵

10^{-4} s⁻¹ calculated according to the reaction scheme above, but including the acid-base equilibrium in eqn. (3). Base-catalysis can therefore be ignored for pH ≤ 9.5.

At higher pH base-catalysis does occur: The reaction of diol in 0.01 M NaOH, 0.99 M NaClO₄ was investigated spectrophotometrically at 25 °C and was shown to give dihydroxo monool quantitatively. The change of absorbance with time obeyed first-order kinetics and gave $k_{\text{obs}} = 2.10(2) \times 10^{-3}$ s⁻¹ [which is 5 times faster than the uncatalyzed reaction (k_1)].

DISCUSSION

The equilibration between the monools and the diol in the present Rh(III) system occurs *via* an acid-catalyzed and an uncatalyzed reaction path, and a similar reaction scheme was recently observed for the first bridge cleavage of the ammonia Cr(III) diol, [(NH₃)₄Cr(OH)₂(NH₃)₄]⁴⁺.^{18,19} This similarity between Rh(III) and Cr(III), however, is no longer apparent if one compares with other bridged Cr(III) complexes; the first bridge cleavage of the two isomers (Δ,Δ-Λ,Λ and Δ,Λ) of [(en)₂Cr(OH)₂Cr(en)₂]⁴⁺ and of the mixed compound Δ,Λ-[(en)₂Co(OH)₂Cr(en)₂]⁴⁺ occurs only *via* an uncatalyzed reaction path.¹⁴⁻¹⁶ Similarly, no acid catalysis has been observed for the bridge-cleavage of the *cis*-aquaerythro cation, [(NH₃)₅Cr(OH)Cr(NH₃)₄(OH₂)]⁵⁺, and for the related anionoerythro complexes.¹¹⁻¹³

The analogous Co(III) complexes exhibit pronounced acid-catalysis.¹⁻⁸ Bridge cleavage of the Co(III) complex [(NH₃)₅Co(OH)Co(NH₃)₅]⁵⁺ has been reported to proceed *via* two reaction paths, an

acid-catalyzed and an uncatalyzed.^{1,2} Acid-catalysis has also been reported for the first bridge cleavage of several trihydroxo-bridged complexes of Co(III), and in fact in these systems an uncatalyzed path was not observed.⁵ Cleavage of the cobalt(III) diols [(NH₃)₄Co(OH)₂Co(NH₃)₄]⁴⁺ and Δ,Λ-[(en)₂Co(OH)₂Co(en)₂]⁴⁺ is acid-catalyzed, although in none of these cases has it been possible to establish with certainty whether the acid-catalyzed path is associated with the first or the second bridge-cleavage, or both.^{3,4}

By analogy with the above-mentioned studies on Co(III) and Cr(III) the acid-catalyzed reaction path in the present Rh(III) system is proposed to involve protonation of one hydroxo bridge to give a labile aqua-bridged intermediate. In the Rh(III), Cr(III) and Co(III) systems the aqua-bridged intermediates are very strong acids with acid dissociation constants much greater than unity, and only the ratio k_2/K_{a3} has been determined. The activation parameters given for the acid-catalyzed path are therefore composite terms, [$\Delta H^\ddagger(k_2) - \Delta H^\circ(K_{a3})$] and [$\Delta S^\ddagger(k_2) - \Delta S^\circ(K_{a3})$]. Since $\Delta H^\circ(K_{a3})$, referring to a very strong acid, is undoubtedly negative²⁶ we obtain as an upper-limit estimate for the Rh(III) system that $\Delta H^\ddagger(k_2) < 58$ kJ mol⁻¹. This reflects, as anticipated, that water is a poor bridging group, and similar low ΔH^\ddagger values have been observed for the Cr(III) and Co(III) complexes.^{5,18,19}

The values for k_{-1} and k_{-2} in the rhodium(III) system are similar, and the corresponding ΔH^\ddagger values are nearly identical. The values for ΔS^\ddagger are also similar. These results suggest that the k_{-1} and k_{-2} paths involve the same mechanism. Both reactions involve replacement of coordinated water, but since coordinated water is a much poorer nucleophile than coordinated hydroxide an essentially associative mechanism would require very different ΔH^\ddagger values, which clearly is not the case.

We therefore propose that the k_{-1} and k_{-2} reactions are both essentially dissociative in character. In both reactions a rate-determining Rh-OH₂ bond-rupture is then assumed to give a transition state in which both coordinated OH (k_{-1}) and coordinated H₂O (k_{-2}) are captured by intramolecular reactions, faster than intermolecular capture of solvent water. Accordingly, we expect k_{-1} and k_{-2} to be similar to k_{ex} for the water-exchange reactions of related hydroxo-bridged complexes (*i.e.* complexes for which intramolecular reactions do not compete with the solvent exchange reaction). However, no such data have been

reported, and we are therefore restricted to data for monomeric complexes.

For water exchange^{27,28} in the pentaammine complex, $[\text{Rh}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$, we have $k_{\text{ex}} = 1.0 \times 10^{-5} \text{ s}^{-1}$ (25 °C, $I = 0.5 \text{ M}$), which is a factor of five less than k_{-1} and k_{-2} . The ΔH^\ddagger values for all three processes are similar (ΔH^\ddagger (exchange) = 101 kJ mol⁻¹). The result seems to support an essentially dissociative mechanism in the case of the bridged complexes. In contrast to this the water exchange of the pentaammine complex is assigned an I_a mechanism.²⁷⁻³¹

Relevant to this discussion is the corresponding chromium(III) ammine system (*i.e.* $[(\text{NH}_3)_4\text{Cr}(\text{OH})_2\text{Cr}(\text{NH}_3)_4]^{4+}$). In the chromium(III) system, ring closure of the monools (k_{-1} and k_{-2}) has been assigned an essentially associative mechanism and the different nucleophilic properties of coordinated OH^- and OH_2 were clearly demonstrated by a large difference between the ΔH^\ddagger values (80.6 and 123 kJ/mol⁻¹, respectively).^{18,19} This difference in associative behaviour of the hydroxo-bridged complexes of Cr(III) and Rh(III) corresponds qualitatively to the observation that for pentaammine complexes the degree of association increases along the series $\text{Co}(\text{NH}_3)_5\text{X} < \text{Ir}(\text{NH}_3)_5\text{X} < \text{Rh}(\text{NH}_3)_5\text{X} < \text{Cr}(\text{NH}_3)_5\text{X}$ (X is a singly charged anion or water).²⁹⁻³²

The influence of ionic strength on the rate constants supports the proposed reaction scheme. For the composite term $k_1 + k_{-1}$ there is no significant change on going from ionic strength 1.0 to 0.1 M. This is a reasonable result since k_1 is associated with a reaction between a cation and a neutral molecule and k_{-1} is associated with an intramolecular reaction. According to conventional reaction rate theory, both reactions should be influenced to a very small extent by the ionic strength.³³

For the composite term k_2/K_{a3} there is a decrease by a factor of 3 on going from ionic strength 1.0 to 0.1 M. Since k_2 is associated with a reaction between a cation and a neutral molecule, its ionic-strength dependency is probably negligible and the change is consequently essentially caused by a change in K_{a3} . This requires that K_{a3} increases by a factor of *ca.* 3 when the ionic strength is decreased from 1.0 to 0.1 M, which is qualitatively in agreement with the behaviour predicted theoretically for a cationic acid.

The difference between the two $\text{p}K_a$ values for the diaqua monool is nearly 7 units. As discussed below, this large difference reflects a simultaneous

decrease in $\text{p}K_{a1}$ and increase in $\text{p}K_{a2}$ relative to what would be expected on the basis of semi-quantitative charge considerations.

From charge considerations alone we expect the acid strength of $\Delta, \Delta - [(\text{H}_2\text{O})(\text{en})_2\text{Rh}(\text{OH})\text{Rh}(\text{en})_2(\text{OH}_2)]^{5+}$ to be greater than that of *cis*- $[\text{Rh}(\text{en})_2(\text{H}_2\text{O})_2]^{3+}$. On the basis of the $\text{p}K_a$ values for *cis*- $[(\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2)]^{3+}$ (4.96)³⁴ and for *cis*- $[(\text{NH}_3)_5\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})]^{5+}$ (3.5)³⁵ we estimate, allowing for a statistical factor of two (0.3 $\text{p}K_a$ units), that the rhodium diaqua monool should be a stronger acid than the monomeric diaqua ion by approximately 1.8 $\text{p}K_a$ units. From the $\text{p}K_a$ values (6.34 and 8.24) of *cis*- $[\text{Rh}(\text{en})_2(\text{H}_2\text{O})_2]^{3+}$ we therefore estimate that the rhodium diaqua monool should have $\text{p}K_{a1} \approx 4.5$ and $\text{p}K_{a2} \approx 6.4$ (upper limit). The observed $\text{p}K_a$ values (2.4 and 9.1) are clearly significantly different from these predicted values and we note that the deviation applies to both $\text{p}K_{a1}$ and $\text{p}K_{a2}$.

A similar increased stability of the aquahydroxo form relative to its acid and base form has also been observed in the corresponding chromium(III) ethylenediamine and ammine systems.¹⁴⁻¹⁹ Following a recent discussion¹⁸ in connection with the chromium(III) systems we propose that the Rh(III) aquahydroxo monool, by analogy with the chromium(III) monools, is stabilized relative to the diaqua and dihydroxo monools by internal hydrogen-bond formation between coordinated water and hydroxide, as shown in Fig. 2. A similar internal hydrogen-bond stabilization might also occur in the diaqua and in the dihydroxo complexes, but the very symmetrical conformation in the aquahydroxo monool, with H_2O donating hydrogen to OH , is likely to be more stable than those of the latter. This hydrogen-bond stabilization can therefore account for the decrease in $\text{p}K_{a1}$ and the increase in $\text{p}K_{a2}$ relative to the values expected purely on the basis of charge considerations.

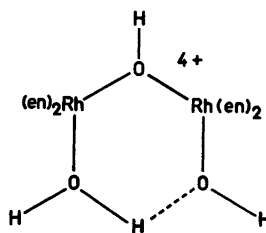


Fig. 2. The proposed hydrogen-bond stabilized structure of the aquahydroxo monool.

EXPERIMENTAL

Materials. The complex $\text{cis-}[\text{Rh}(\text{en})_2\text{Cl}_2]\text{-Cl}_3(\text{ClO}_4)_3$ was prepared as described previously.²⁴ All chemicals were of analytical grade.

Instruments. A Zeiss DMR 21 spectrophotometer was used for all spectrophotometric measurements in the visible region. Data are given with the molar decadic absorption coefficient ϵ in $1 \text{ mol}^{-1} \text{ cm}^{-1}$ 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 rhodium(III) per litre of solution.

The pH measurements were made with a Radiometer GK 2301 C combined glass and calomel electrode in conjunction with a Radiometer PHM 61 digital pH-meter.

Analyses. C, H, N, Br and Cl analyses were performed by the microanalytical laboratory at the H. C. Ørsted Institute, Copenhagen.

Potentiometric measurements. The pH measurements at 25 °C were made as described previously in connection with the corresponding chromium(III) systems,¹⁴⁻¹⁹ and the definition $\text{pH} = -\log[\text{H}^+]$ was employed throughout. The determination of $\text{p}K_{a1}$ of the diaqua monool at 35.0 °C was made using equilibrium conditions as described in the following.

Partly neutralized solutions of the aquahydroxo monool salt were kept at 35.0 °C and pH was monitored. The pH initially decreased with time due to the formation of diol and became constant after 15 min, showing that equilibrium had been attained. From the $[\text{H}^+]$ measured at equilibrium, $\text{p}K_{a1}$ can be calculated using standard procedures if corrections are made for the small content (~10 %) of diol. Such corrections can be made if K_1 is known. However, the spectrophotometric determination of K_1 requires a knowledge of K_{a1} , and the calculations of K_{a1} and of K_1 were therefore made simultaneously using iteration. Only one iteration was necessary.

Spectra and treatment of spectral data. Spectra of monool and of diol salts in different media, extrapolated to the time of dissolution and at equilibrium, were obtained as described recently.¹⁹ Pseudo first-order rate constants, k_{obs} , and activation parameters were calculated as described previously.¹⁹ The k_{obs} values were calculated from absorbances measured at two or three of the wavelengths $\lambda = 330, 300$ and 280 nm (for solutions initially containing diol) or $\lambda = 254, 250, 246,$ and 242 nm (for solutions initially containing monool). All kinetic runs were performed in duplicate.

In all kinetic runs the hydrogen ion concentration changed slightly. These changes were generally about 1–3 %, although in experiments with low

$[\text{H}^+]$, changes of up to 8 % were calculated [eqns. (1) and (2)]. However, the error introduced by this variation is very small, since at low $[\text{H}^+]$ the dependence of k_{obs} on $[\text{H}^+]$ is small. For each experiment the hydrogen ion concentrations at t_0 , $[\text{H}^+]_0$, and at equilibrium, $[\text{H}^+]_{\infty}$, were calculated and the values $[\text{H}^+] = \frac{1}{2}([\text{H}^+]_0 + [\text{H}^+]_{\infty})$, were then used in the subsequent calculations.

The calculations of K_1 were based on absorbances of solutions of pure diol, ϵ_D , pure monool, ϵ_M , and the equilibrium solution, ϵ_{∞} , measured at $\lambda = 254, 250, 246$ and 242 nm and using eqn. (6).

$$K_1 = \frac{(\epsilon_D - \epsilon_{\infty})}{(\epsilon_{\infty} - \epsilon_M)} \frac{K_{a1}}{[\text{H}^+] + K_{a1}} \quad (6)$$

The ratio $(\epsilon_D - \epsilon_{\infty})/(\epsilon_{\infty} - \epsilon_M)$ is experimentally difficult to measure since the equilibrium is shifted very much toward monool and accordingly the relative difference between ϵ_{∞} and ϵ_M is very small. This difference is greatest in weakly acid solution, for which the ratio is approximately equal to K_1 and the measurements were therefore made in solutions with $[\text{HClO}_4] = 10^{-3}, 5 \times 10^{-4}$ and 10^{-4} M , respectively.

The value of K_1 at 25 °C was then calculated using the value for K_{a1} determined as above. As discussed above, the calculations of K_1 and K_{a1} at the higher temperatures were made simultaneously, using iteration.

Preparations

1. *cis-Aquabis(ethylenediamine)hydroxorhodium(III) dithionate, cis-}[\text{Rh}(\text{en})_2(\text{OH})(\text{H}_2\text{O})]\text{S}_2\text{O}_6. *cis-}[\text{Rh}(\text{en})_2\text{Cl}_2]\text{Cl}_3(\text{ClO}_4)_3 (6.0 g; 16.60 mmol) and AgNO_3 (8.57 g; 50.45 mmol) were heated under reflux for 3 h in water (50 ml) in the dark. The reaction mixture was allowed to stand overnight. 1.00 M HCl (11.0 ml) was added, and after standing for ca. 10 min the solution was filtered. The flask and funnel were rinsed with boiling water ($3 \times 10 \text{ ml}$) and the filtered washings added to the bulk filtrate. Finely powdered $\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ (6.0 g) was added and dissolved by stirring at room temperature. Then 1.00 M NaOH (24 ml) was added and a finely-divided pale-yellow precipitate was formed. After leaving the mixture to stand for ca. 1 h at room temperature and then in an ice-bath for ca. 20 min, the product was isolated by filtration, washed with ice-cold water, then 96 % ethanol and ether and air-dried. Yield 5.32 g (77 %).**

The pure product was obtained by reprecipitation. Crude aquahydroxo dithionate (2.0 g; 4.78 mmol) and finely powdered $\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ (2.4 g)

were stirred together in 0.50 M HCl (12.0 ml) until all was dissolved. 1.0 M NaOH was then added dropwise to the stirred, filtered solution to give pH=7, when a pale-yellow precipitate formed rapidly. After stirring at room temperature for ca. 15 min the mixture was kept in an ice-bath for 45 min and then filtered. Washing and drying were performed as before. Yield 1.88 g (94 %). The product reprecipitated twice in this manner showed no changes in the UV-visible absorption spectrum on further reprecipitation. Anal. $[\text{Rh}(\text{en})_2(\text{OH})-(\text{H}_2\text{O})]\text{S}_2\text{O}_6$: C, H, N. Spectral data (0.1 M HClO_4 , 0.9 M NaClO_4 ; 25 °C) $(\epsilon, \lambda)_{\text{max}}$: (175,317), (137,271). $(\epsilon, \lambda)_{\text{min}}$: (117,289), (32,236).

2. Δ, Λ -Di- μ -hydroxobis[bis(ethylenediamine)-rhodium(III)]bromide dihydrate, Δ, Λ - $[(\text{en})_2\text{Rh}(\text{OH})_2\text{Rh}(\text{en})_2]\text{Br}_4 \cdot 2\text{H}_2\text{O}$. Crude diol dithionate (4.81 g; 6.01 mmol) was stirred vigorously in saturated NH_4Br solution (55 ml) at room temperature for 1 h. The resulting crude bromide salt was then isolated by suction filtration on a fine-porosity sintered glass funnel and washed with ice-cold 1:1 aqueous ethanol. The product was extracted on the filter with water (temp. 20 °C) in portions within a total of 20 min (total extraction volume ca. 200 ml) and the portions of solution were filtered immediately into an ice-cooled 500 ml conical flask containing stirred NH_4Br solution (80 ml, saturated at room temp.). A dense pale-yellow precipitate was immediately formed, and after cooling with stirring for a further 20 min the product was isolated by filtration, washed with ice-cold 1:1 aqueous ethanol, then 96 % ethanol and finally ether, and air-dried. Yield 3.85 g (77 %). Anal. $[\text{Rh}_2(\text{en})_4(\text{OH})_2]\text{Br}_4 \cdot 2\text{H}_2\text{O}$: C, H, N, Br.

3. Δ, Λ -Di- μ -hydroxobis[bis(ethylenediamine)-rhodium(III)]perchlorate, Δ, Λ - $[(\text{en})_2\text{Rh}(\text{OH})_2\text{Rh}(\text{en})_2](\text{ClO}_4)_4$. Δ, Λ - $[(\text{en})_2\text{Rh}(\text{OH})_2\text{Rh}(\text{en})_2]\text{Br}_4 \cdot 2\text{H}_2\text{O}$ (3.85 g) was stirred vigorously with a mixture of saturated NaClO_4 (20 ml) and water (20 ml) at ca. 16 °C for 1 h. The precipitate was filtered off by suction on a fine-porosity sintered glass funnel, washed with 96 % ethanol and sucked almost dry. The product was then extracted on the filter with water (ca. 16 °C) in small portions within a total of 7 min (total volume ca. 70 ml) and the portions filtered immediately into an ice-cooled flask containing stirred NaClO_4 solution (50 ml, saturated at room temp.). After cooling and stirring for a further 15 min the product was isolated by filtration, washed with 96 % ethanol and then ether, and air-dried. Yield. 3.70 g (91 %). Anal. $[\text{Rh}_2(\text{en})_4(\text{OH})_2](\text{ClO}_4)_4$: C, H, N, Cl. The spectral data (Table 1) for this salt are identical with those for the bromide dihydrate, which is strong evidence for the purity of the products.

4. Δ, Λ -Aquatetakis(ethylenediamine)- μ -hydroxohydroxo dirhodium(III) perchlorate, Δ, Λ - $[(\text{H}_2\text{O})-$

$(\text{en})_2\text{Rh}(\text{OH})\text{Rh}(\text{en})_2(\text{OH})](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$. Δ, Λ - $[(\text{en})_2\text{Rh}(\text{OH})_2\text{Rh}(\text{en})_2](\text{ClO}_4)_4$ (3.0 g, 3.42 mmol) was added to water (9.0 ml) at 55.0 ± 0.5 °C and the stirred mixture was kept at that temperature for 20 min. All the complex dissolved within the first 3 min. The solution was then cooled in ice and a saturated (at 20 °C) solution of sodium perchlorate (9 ml) was added. After 20 min the precipitate was filtered off and washed thoroughly with 96 % ethanol. Drying in air gave 2.80 g of crude aquahydroxo monool salt. The crude perchlorate salt (2.8 g) was dissolved in 1.000 M perchloric acid (10.00 ml) at 25.0 ± 0.1 °C within 30 s. After a further 120 s the filtered solution was cooled in ice and a saturated solution of sodium perchlorate (15 ml) added. After a further ca. 10 min the almost colourless solution was filtered and then 2.00 M sodium hydroxide (5.00 ml) was added. The aquahydroxo monool salt precipitated within a few minutes and was isolated as above. Yield 2.50 g (80 %) of a pure salt. Further reprecipitation did not change the absorption spectrum in the region 350–240 nm. Anal. $[\text{Rh}_2(\text{en})_4(\text{H}_2\text{O})(\text{OH})_2](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$: C, H, N, Cl.

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REFERENCES

- Wharton, R. K. and Sykes, A. G. *J. Chem. Soc. Dalton Trans.* (1973) 439.
- Buckingham, D. A., Marty, W. and Sargeson, A. M. *Inorg. Chem.* 13 (1974) 2165.
- Ellis, J. D., Scott, K. L., Wharton, R. K. and Sykes, A. G. *Inorg. Chem.* 11 (1972) 2565.
- Meloon, D. R. and Harris, G. M. *Inorg. Chem.* 16 (1977) 434 and references therein.
- Wieghardt, K., Schmidt, W., Nuber, B. and Weiss, J. *Chem. Ber.* 112 (1979) 2220 and references therein.
- Laier, T. and Springborg, J. *Acta Chem. Scand.* A 35 (1981) 145.
- Sykes, A. G. and Weil, J. A. *Prog. Inorg. Chem.* 13 (1970) 1.
- Taylor, R. S. and Sykes, A. G. *Inorg. Chem.* 13 (1974) 2824.
- Thompson, G. Report UCRL-11410, Lawrence Radiation Laboratory, Berkeley 1964.
- Wolcott, D. and Hunt, J. B. *Inorg. Chem.* 7 (1968) 755.
- Hoppenjans, D. W. and Hunt, J. B. *Inorg. Chem.* 8 (1969) 505.

12. Po, H. N. and Enomoto, H. *J. Inorg. Nucl. Chem.* 35 (1973) 2581.
13. Po, H. N., Chung, Y. H. and Davis, S. R. *J. Inorg. Nucl. Chem.* 35 (1973) 2849.
14. Springborg, J. and Toftlund, H. *Acta Chem. Scand. A* 30 (1976) 171.
15. Christensson, F., Springborg, J. and Toftlund, H. *Acta Chem. Scand. A* 34 (1980) 317.
16. Springborg, J. and Schäffer, C. E. *Inorg. Chem.* 15 (1976) 1744.
17. Springborg, J. and Schäffer, C. E. *Acta Chem. Scand. A* 30 (1976) 787.
18. Christensson, F. and Springborg, J. *Poster, XXI ICCG*, Toulouse, 7–11th July, 1980. Proceedings 217.
19. Christensson, F. and Springborg, J. *Acta Chem. Scand. A* 36 (1982) 21.
20. Kaas, K. *Acta Crystallogr. B* 35 (1979) 1603.
21. Wiegardt, K., Schmidt, W., Eldik, R., Nuber, B. and Weiss, J. *Inorg. Chem.* 19 (1980) 2922.
22. Hancock, M. P. *Acta Chem. Scand. A* 33 (1979) 499.
23. Springborg, J. and Schäffer, C. E. *Inorg. Synth.* 18 (1978) 75.
24. Hancock, M. P. *Acta Chem. Scand. A* 33 (1979) 15.
25. Palmer, D. A., Eldik, R., Kelm, H. and Harris, G. M. *Inorg. Chem.* 19 (1980) 1009.
26. Bell, P. P. *The Proton in Chemistry*, Chapman and Hall, London 1973, 2nd Ed.
27. Monacelli, F. and Viel, E. *Inorg. Chim. Acta* 1 (1967) 467.
28. Bott, H. L., Poë, A. J. and Shaw, K. *J. Chem. Soc. A* (1970) 1745.
29. Swaddle, T. W. and Stranks, D. R. *J. Am. Chem. Soc.* 94 (1972) 8357.
30. Gattegno, D. and Monacelli, F. *Inorg. Chim. Acta* 7 (1973) 370.
31. Tong, S. B. and Swaddle, T. W. *Inorg. Chem.* 13 (1974) 1538.
32. Mønsted, L. *Acta Chem. Scand. A* 32 (1978) 377.
33. Frost, A. A. and Pearson, R. G. *Kinetics and Mechanism*, Wiley, New York 1961, 2nd Ed.
34. Mønsted, L. and Mønsted, O. *Acta Chem. Scand. A* 30 (1976) 202.
35. Bjerrum, J., Schwarzenbach, G. and Sillén, L. G. *Stability Constants of Metal-Ion Complexes*. The Chemical Society, 2nd Ed., London 1964, 3rd. Ed., London 1971.

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