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Cleavage and Formation of Hydroxo-Bridged Binuclear Rhodium(III) Ethylenediamine Complexes

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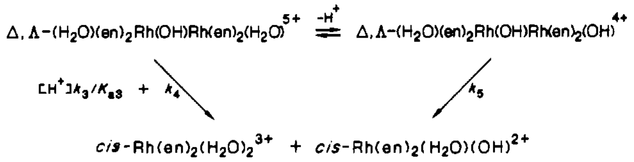
The kinetics of the cleavage of monohydroxo-bridged binuclear rhodium(III) complexes in acidic solution to give mononuclear species have been studied spectrophotometrically. The results are interpreted in terms of uncatalyzed (k_4 and k_5) and acid-catalyzed (k_3/K_{a3}) reaction paths (see also Scheme I)



and the kinetic parameters determined to be as follows (k at 25.0 °C, $\Delta H^{\ddagger}$ in kJ mol^{-1}, and $\Delta S^{\ddagger}$ in J mol^{-1} deg^{-1}): $k_5 = 2.30$ (10) $\times 10^{-7}$ s^{-1}, $\Delta H^{\ddagger} = 107$ (2), $\Delta S^{\ddagger} = -12$ (6); $k_4 = 3.82$ (15) $\times 10^{-6}$ s^{-1}, $\Delta H^{\ddagger} = 116$ (3), $\Delta S^{\ddagger} = 40$ (10); $k_3/K_{a3} = 3.48$ (15) $\times 10^{-5}$ M^{-1} s^{-1}, $\Delta H^{\ddagger} = 78$ (4), $\Delta S^{\ddagger} = -68$ (14). The equilibrium between mono- and dinuclear species has also been studied, and the value of the composite term K_D = [dinuclear]/[*cis*-$Rh(en)_2(H_2O)(OH)^{2+}]^2$ has been determined ([dinuclear] = $[(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)^{4+}] + [(en)_2Rh(OH)_2Rh(en)_2{}^{4+}]$); $K_D = 52$ (8) M^{-1} at 25.0 °C. From this constant together with the kinetic data for the cleavage reaction it is possible to obtain approximate values for the second-order rate constants for the condensation processes.

Introduction

An important feature of the hydrolytic behavior of metal aqua ions is the formation of hydroxy-bridged polynuclear species.[1] One very common structure is $L_4M(OH)_2ML_4{}^{n+}$, which has been characterized for many metal aqua ions. In acidic solution, hydrolysis of the hydroxo-bridged species to give the corresponding mononuclear species is normally complete. Kinetic studies of such cleavage reactions have been reported for a number of cobalt(III) and chromium(III) species, but in most cases the conclusions drawn from these studies are ambiguous with regard to the postulated mechanisms, and the occurrence of conflicting reports concerning the observed rate laws has also complicated the issue.[2-8] A major problem has been the fact that the presumed singly bridged intermediates are apparently unstable with respect to both the dihydroxo-bridged species and the mononuclear species, so that isolation and characterization of these intermediates have in general been unsuccessful. These difficulties do not arise in the case of dihydroxo-bridged ammonia and ethylenediamine complexes of chromium(III), rhodium(III), and iridium(III), for which the first bridge cleavage is orders of magnitude faster than the second.[9-14] In the latter systems the thermodynamic and kinetic stability of the monohydroxo-bridged intermediates has made it possible to isolate and characterize these complexes as crystalline salts, so that a successful study of the kinetics and thermodynamics of the equilibrium between the monohydroxo- and dihydroxo-bridged species has been possible.

As a continuation of these studies we have begun to investigate the cleavage reactions of the monohydroxo-bridged species, and we describe here the results for the rhodium(III) ethylenediamine system. The present work, together with our previous results[13] for the first bridge cleavage, appears to be the first example of a detailed kinetic study of this type of reaction.

Experimental Section

Materials and Instruments. The complexes Δ,Λ-$[(en)_2Rh(OH)_2Rh(en)_2](ClO_4)_4$ and *cis*-$[Rh(en)_2(OH)(H_2O)]S_2O_6$ were synthesized as described previously.[13,15] All reagents were of analytical grade. CO_2-free doubly deionized water was used for all spectrophotometric measurements, which were made on a Zeiss DMR 21 spectrophotometer. The molar absorption coefficient ϵ is given in L (mol of Rh(III))$^{-1}$ cm^{-1} for both mononuclear and dinuclear species, and the wavelength λ is given in nm. 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).

Preparation of *cis*-Aquahydroxobis(ethylenediamine)rhodium(III) Perchlorate, *cis*-$[Rh(en)_2(H_2O)(OH)](ClO_4)_2$. *cis*-$[Rh(en)_2(H_2O)(OH)]S_2O_6$ (1 g, 2.39 mmol) was dissolved at room temperature in a mixture of 50 mL of water and 60 mL of a saturated aqueous solution of $NaClO_4$. Precipitation of the perchlorate salt began within a few minutes, and after 30 min the precipitate was collected on a filter, redissolved in water (20 mL), and reprecipitated by addition of a saturated aqueous solution of $NaClO_4$ (20 mL). The precipitate was isolated by filtration, washed with 96% ethanol and then diethyl ether, and dried in the air; yield 0.83 g (76%). The absorption spectra of the perchlorate and dithionate[13,15] salts in 1.0 M $NaClO_4$ were identical.

Kinetic Measurements. Reactant solutions were made by dissolving Δ,Λ-$[(en)_2Rh(OH)_2Rh(en)_2](ClO_4)_4$ in 1 M (Na,H)ClO_4 solution. Since the reaction has half-lives of between several hours and several months, each kinetic run was normally based on different portions of the same batch of solution, kept separately in glass ampules in the dark.

The hydrogen ion concentration changed slightly during a kinetic experiment. The hydrogen ion concentration in the initial equilibrated solutions of dinuclear species and in the final solutions of mononuclear species, $[H^+]_0$ and $[H^+]_\infty$, respectively, were calculated by using the thermodynamic parameters given in ref 13 and knowing the initial solution stoichiometry. The average values, $[H^+]_{av} = {}^1/_2([H^+]_0 + [H^+]_\infty)$, were used for the calculations of k_{calcd} (eq 1). For solutions with $[H^+]_{av} \geq 10^{-2}$ M the variations in the hydrogen ion concentration were always small, typically 0.1–2%. At lower $[H^+]$ larger variations were calculated (5% and 37.7%, respectively, for $[H^+]_{total}$ = 0.005 and 0.001 M), but in this $[H^+]$ region the observed dependence of k_{obsd} on $[H^+]$ is small. For solutions in pure 1 M $NaClO_4$ it was checked by glass-electrode measurements that the pH was about 6–7 during the entire experiment. It is therefore concluded that the variations in $[H^+]$ can be ignored and that

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Table I. Kinetic Data for Acid-Catalyzed (k_H) and Uncatalyzed (k_0) Cleavage of Monohydroxo-Bridged Rhodium(III) Complexes[a]

complex	$k_0{}^b/\mathrm{s}^{-1}$	$\Delta H^*/\mathrm{kJ\ mol}^{-1}$	$\Delta S^*/\mathrm{J\ mol}^{-1}\ \mathrm{K}^{-1}$	$k_H{}^c/\mathrm{M}^{-1}\ \mathrm{s}^{-1}$	$\Delta H^*/\mathrm{kJ\ mol}^{-1}$	$\Delta S^*/\mathrm{J\ mol}^{-1}\ \mathrm{K}^{-1}$
$\Delta,\Lambda\text{-}(H_2O)(en)_2Rh(OH)Rh(en)_2(H_2O)^{5+}$	$3.82\ (15) \times 10^{-6}$	116 (3)	40 (10)	$3.48\ (15) \times 10^{-5}$	78 (4)	−68 (14)
$\Delta,\Lambda\text{-}(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)^{4+}$	$2.30\ (10) \times 10^{-7}$	107 (2)	−12 (6)			

[a] At 25 °C and $I = 1.0$ M ((Na,H)ClO$_4$). One standard deviation is given in parentheses. [b] k_0 is equal to k_4 or k_5 in Scheme I. [c] k_H is equal to k_3/K_{a3} in Scheme I; $\Delta H^* = \Delta H^*(k_3) - \Delta H^\circ(K_{a3})$; $\Delta S^* = \Delta S^*(k_3) - \Delta S^\circ(K_{a3})$.

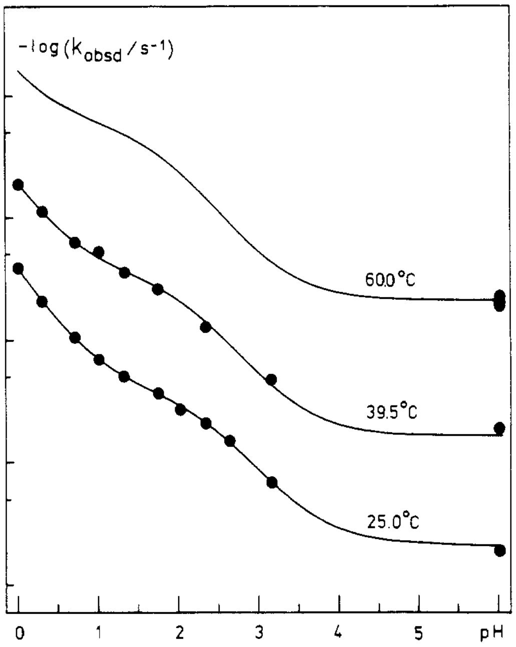


Figure 1. Plots of observed pseudo-first-order rate constants, k_{obsd}, as a function of pH = −log [H$^+$]. The solid lines represent values of k calculated by eq 1 with use of the parameters given in Table I and the values of $K_{a1}{}^d$ and K_1 given in ref 13. At 60 °C k_{obsd} was measured at pH 6 for $C_{Rh(III)}$ varying from 6×10^{-5} to 6×10^{-4} M.

pseudo-first-order conditions can be assumed.

Pseudo-first-order rate constants, k_{obsd}, were calculated from the absorbance A as a function of time t by means of nonlinear regression analysis, with use of the expression $A = A_\infty + (A_0 - A_\infty) \exp(-k_{obsd}t)$, where A_0 is the absorbance at $t = 0$ and A_∞ is the absorbance at completion. The rate constants were calculated on the basis of absorbances measured at the wavelengths 330, 300, and 270 nm, and $A_0 - A_\infty$ values were from 0.2 to 0.4.

The activation parameters ΔH^* and ΔS^* for k_3/K_{a3}, k_4, and k_5 were fitted by minimizing $\sum(\ln k_{obsd} - \ln k_{calcd})^2$, the values of k_{calcd} being defined by eq 1 in combination with the expression $k_r = (kT/h) \times \exp(\Delta S^*/R - \Delta H^*/RT)$ (Table I, Figure 1).

Determination of the Dimerization Constant K_D. Spectrophotometric Determination. The stoichiometric equilibrium defined in eq 2 was studied spectrophotometrically for 1 M NaClO$_4$. Solutions of either Δ,Λ-[(en)$_2$Rh(OH)$_2$Rh(en)$_2$](ClO$_4$)$_4$ or *cis*-[Rh(en)$_2$(H$_2$O)(OH)](ClO$_4$)$_2$ in 1 M NaClO$_4$ were kept in glass ampules at 60, 80, and 100 °C for 70, 8, and 1 h, respectively. Subsequent heating produced only negligible changes in the spectra, and for a given $C_{Rh(III)}$, the spectra were identical for solutions initially containing pure dinuclear and mononuclear species, respectively. The equilibrium constant, K_D, was calculated from the expression $K_D = (\epsilon_m - \epsilon_d)(\epsilon_m - \epsilon_\infty)/(2C_{Rh}(\epsilon_\infty - \epsilon_d)^2)$, where ϵ_d, ϵ_m, and ϵ_∞ are molar absorbances for solutions containing an equilibrium mixture of the dinuclear species (ϵ_d), pure mononuclear species (ϵ_m), and mono- and dinuclear species in equilibrium (ϵ_∞). The calculations were made on the basis of ϵ values measured at wavelengths λ = 260–280 nm. In all experiments the rhodium(III) concentration was 10^{-2} M and the values of K_D were found to be independent of the wavelength.

Determination by Titration. Equilibrium solutions were made as described above, and the rhodium(III) concentration was varied as shown in Table II. The concentration of mononuclear species was determined by potentiometric titration with perchloric acid, and this gave K_D.

Results

Kinetics of the Cleavage of Singly Bridged Species. The Δ,Λ-(en)$_2$Rh(OH)$_2$Rh(en)$_2{}^{4+}$ ion undergoes bridge cleavage in acidic solution to give the mononuclear species *cis*-Rh(en)$_2$(H$_2$O)$_2{}^{3+}$ and *cis*-Rh(en)$_2$(H$_2$O)(OH)$^{2+}$. Bridge cleavage occurs in two rather slow and kinetically well-separated steps, which makes this system an obvious candidate for detailed kinetic and thermodynamic studies.

Equilibration between the monohydroxo- and dihydroxo-bridged species in acidic solution has previously been shown to involve the equilibria shown in the upper part of Scheme I.[13] The aim of the present study was primarily to investigate the hydrolysis of the monohydroxo-bridged species to give the mononuclear complexes. The reaction was studied spectrophotometrically at three temperatures (25.0, 39.5, and 60.0 °C), and the hydrogen ion concentration was varied from 1.0 M to approximately 10^{-6} M while a constant ion strength of 1.00 M ((Na,H)ClO$_4$) was maintained. Reactant solutions were obtained by dissolving Δ,Λ-[(en)$_2$Rh(OH)$_2$Rh(en)$_2$](ClO$_4$)$_4$ in the appropriate medium and then allowing the solutions to equilibrate with respect to the monohydroxo- and dihydroxo-bridged species before the kinetic measurements were started. The latter equilibration is about 10^3 times faster than the second bridge cleavage over the entire [H$^+$] region,[13] and it therefore follows that the monohydroxo-bridged species are in equilibrium with the dihydroxo-bridged species throughout the entire reaction.

The reaction entails consumption of H$^+$ ions, and [H$^+$] values used were such that the change in [H$^+$] during the reactions was generally less than 2%. The change in absorbance with time followed first-order kinetics throughout the entire reaction.

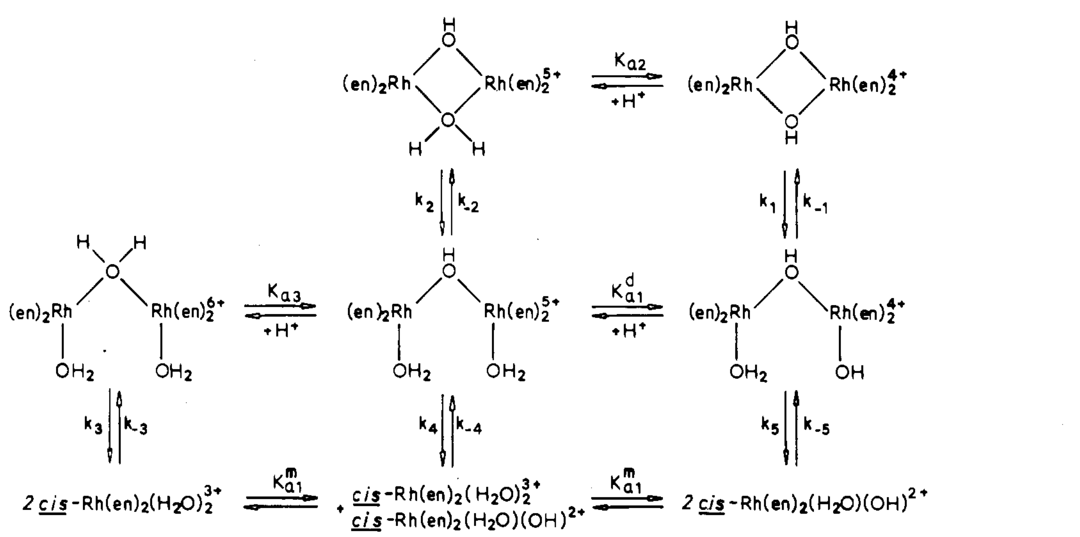
The visible–ultraviolet spectra of the final product solutions were compared with the spectra of solutions of *cis*-[Rh(en)$_2$(H$_2$O)(OH)]S$_2$O$_6$ in 1 M (Na,H)ClO$_4$ and at a hydrogen ion concentration identical with those of the hydrolyzed solutions. For solutions with [H$^+$] = 10^{-3}–1.0 M the spectra showed that hydrolysis to mononuclear species is quantitative, irrespective of the rhodium(III) concentration. For solutions with [H$^+$] = 10^{-6}–10^{-3} M the spectra also indicated quantitative formation of mononuclear species (>95% completion), but only when the complex concentration was low (see also the next paragraph). The kinetic measurements at low [H$^+$] were therefore all made at rhodium(III) concentrations so low that the formation of mononuclear species is stoichiometrically quantitative. The reverse reactions can therefore be ignored, and this was further substantiated by the fact that k_{obsd} values were independent of rhodium(III) concentrations varying from 6×10^{-5} to 6×10^{-4} M. A listing of the observed and calculated rate constants is given in the supplementary material; see also Figure 1.

The reaction rate is pH-dependent, with a half-life at 25.0 °C of 42 days at [H$^+$] ≈ 10^{-6} M and 5 h at [H$^+$] = 1.0 M. The observed [H$^+$] dependence is consistent with Scheme I, which shows the reaction scheme proposed previously for the equilibration between monohydroxo- and dihydroxo-bridged species supplemented with the possible depolymerization reactions. According to this scheme the rate of cleavage into mononuclear species is calculated to be as given by eq 1, since protonation of the mo-

$$k_{calcd} = \frac{(k_3/K_{a3})[H^+]^2 + k_4[H^+] + k_5K_{a1}{}^d}{[H^+] + K_{a1}{}^d/K_1 + K_{a1}{}^d} \qquad (1)$$

nohydroxo-bridged diaqua species is stoichiometrically negligible; i.e., $K_{a3} >> [H^+]$.[13] The equilibrium constants $K_1 = k_1/k_{-1}$ and $K_{a1}{}^d$ have been determined previously; K_1 = 11.2 (5) and $K_{a1}{}^d$ = 4.25 (7) × 10^{-3} M at 25.0 °C.[13] Values at higher temperatures were calculated from the ΔH° and ΔS° values given in ref 13. The remaining three parameters (k_3/K_{a3}, k_4, and k_5) and their activation parameters were calculated by the method of nonlinear regression analysis, giving the values reported in Table I. From

Scheme I. Reaction Scheme for the Acid Hydrolysis of the Meso Isomers $\Delta,\Lambda\text{-}(en)_2Rh(OH)_2Rh(en)_2{}^{4+}$ and $\Delta,\Lambda\text{-}(H_2O)(en)_2Rh(OH)Rh(en)_2(H_2O)^{5+}$



the curvature of Figure 1 it is clear that at least three kinetic parameters are required to describe the dependence of k_{obsd} on pH. In addition it is noted that each of the parameters contribute significantly to k_{obsd}: from the parameters given in Table I and the K_1 and K_{a1} values given above it can be calculated that k_3/K_{a3}, k_4, and k_5, respectively, at 25.0 °C contribute to k_{obsd} by factors of 90%, 10%, and 0% at $[H^+] = 1.0$ M, by 8%, 90%, and 2% at $[H^+] = 0.01$ M, and by 0%, 0%, and 100%, respectively, at $[H^+] = 10^{-6}$ M. Similar ratios are found for 39.5 and 60.0 °C. The parameters are thus seen to be well-defined by the k_{obsd} values in the pH region investigated. This is further emphasized by the magnitude of standard deviations given in Table I.

Thermodynamic Studies. The equilibrium between *cis*-$Rh(en)_2(H_2O)(OH)^{2+}$ and the monohydroxo- and dihydroxo-bridged species in 1 M $NaClO_4$ was studied for the temperatures 60.0, 80.0, and 100.0 °C. Equilibrated solutions were obtained by heating solutions initially containing either the mononuclear or dinuclear species for 70, 8, and 1 h, respectively. The equilibrated solutions were quenched by cooling to 25.0 °C, at which temperature the half-life, as mentioned, is 42 days. The quenched solutions were then analyzed at 25.0 °C by potentiometric titration with acid and by spectrophotometric measurements. The fact that the same results were obtained for solutions initially containing pure mononuclear and dinuclear species, respectively, confirmed that equilibrium had been attained. The results obtained by both methods were consistent with eq 2, in which mononuclear is

$$2\ \text{mononuclear} \overset{K_D}{\rightleftharpoons} \text{dinuclear} \qquad (2)$$

cis-$Rh(en)_2(H_2O)(OH)^{2+}$ and dinuclear is both $(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)^{4+}$ and $(en)_2Rh(OH)_2Rh(en)_2{}^{4+}$. In the former method the content of the mononuclear species was determined by potentiometric titration with perchloric acid, which is straightforward since the mononuclear diaqua species has $pK_{a1}{}^{m} = 6.3$ and the dinuclear species exhibit no acid–base properties in this pH region. The spectrophotometric determination was made on the basis of measurements at 260–280 nm, at which wavelengths there is a very large difference between the absorbancies of the mononuclear ($\epsilon \approx 100$ M^{-1} cm^{-1}) and the dinuclear ($\epsilon \approx 300$ M^{-1} cm^{-1}) species. It should be noted that the spectrophotometric measurements showed that isomerization of *cis*- to *trans*-$Rh(en)_2(H_2O)(OH)^{2+}$ is negligible under the conditions employed in this study.

Although the results of both studies can be interpreted in terms of stereospecific formation of the known meso isomers (Δ,Λ) of the binuclear species, the possibility that a significant amount of the as yet uncharacterized racemic ($\Delta,\Delta/\Lambda,\Lambda$) isomer is also formed cannot be excluded. The spectroscopic and acid–base properties of the two pairs of isomers are likely to be very similar, and the presence of an additional isomer would therefore not be detected by either of the two methods. However, the fact that identical K_D values have been obtained by the two methods seems to confirm that the interpretation in terms of eq 2 (including the possible presence of two isomers) is correct (Table II). Attempts to separate the presumed mixture of meso and racemic isomers have so far been without success. Plots of ln K_D against $1/T$ gave a straight line, but it should be noted that since K_D may be a composite term, it is not necessarily required that such a relationship should apply. Interpretation in terms of $\ln K_D = \Delta S°/R - \Delta H°/RT$ gave the values $\Delta H°(K_D) = -14.4$ (20) kJ mol^{-1} and $\Delta S°(K_D) = -15$ (6) J mol^{-1} K^{-1}, from which the value $K_D = 52$ (8) M^{-1} at 25 °C is calculated. Interpretation of K_D in terms of a true equilibrium constant is discussed below.

Table II. Determination of the Condensation Constant K_D[a]

T/ °C	K_D(H$^+$ titration)/ M^{-1}	K_D(spectrophotometric)[c]/ M^{-1}	K_D(calcd)[d]/ M^{-1}
100	15.7[b]	18.5	16.3
80	21.3[c]	22.5	21.2
60	27.2[c]	29.2	28.5

[a] With 1 M $NaClO_4$; K_D defined in eq 2. [b] Average of six determinations with $C_{Rh(III)} = 0.005$–0.1 M. [c] Average of two determinations with $C_{Rh(III)} = 0.02$ M. [d] Calculated by using $\Delta H° = -14.4$ (20) kJ mol^{-1} and $\Delta S° = -15$ (6) J mol^{-1} K^{-1}, which gives $K_D = 52$ (8) M^{-1} at 25 °C.

Discussion

The interpretation of the kinetic data in terms of uncatalyzed (k_0) and acid-catalyzed (k_H) bridge cleavage is in keeping with previous studies of other hydroxo-bridged dirhodium(III) systems (in the present case k_0 is equal to k_4 or k_5 and k_H is equal to k_3/K_{a3}, as shown in Scheme I).[12,13,16] It should be noted that the present data do not distinguish between the proposed reaction path involving uncatalyzed cleavage of the diaqua ion (k_4) and acid-catalyzed cleavage of the deprotonated ion $\Delta,\Lambda\text{-}(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)^{4+}$; the latter path is, however, ignored in the following discussion.

Following the previous studies,[12,13] the acid-catalyzed path is proposed to involve protonation of the hydroxo bridge leading to a labile aqua-bridged intermediate that is a strong acid ($K_{a3} >$ 1 M). Similarly, strongly acidic and labile aqua-bridged intermediates have also been proposed for several hydroxo-bridged cobalt(III), iridium(III), and chromium(III) complexes,[2-14,17-20]

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Table III. Ratios between the Rate Constants of Acid-Catalyzed (k_H) and Uncatalyzed (k_0) Bridge-Cleavage Reactions[a]

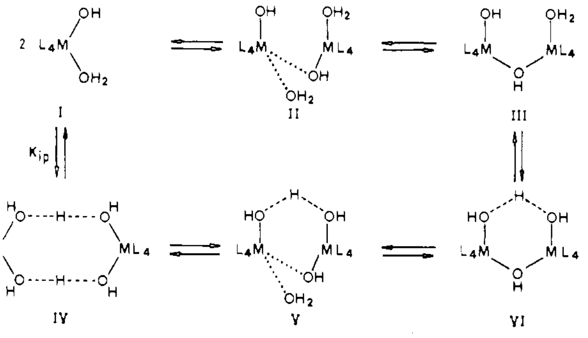
complex	$(k_H/k_0)/M^{-1}$ Co(III)	Rh(III)	Ir(III)	Cr(III)	ref
$(NH_3)_3M(OH)_3M(NH_3)_3^{3+}$	>1000[b]				17
Δ,Λ-$(en)_2M(OH)_2M(en)_2^{4+}$		294	162	<0.05[c]	9, 13, 14
$(NH_3)_4M(OH)_2M(NH_3)_4^{4+}$		1740		0.4	11, 12
$(NH_3)_5M(OH)M(NH_3)_5^{5+}$	1.55			<0.01[c]	19, 20, 23
Δ,Λ-$(H_2O)(en)_2M(OH)M(en)_2(H_2O)^{5+}$		9.1			this work
$(H_2O)_2(tacn)M(OH)M(tacn)(H_2O)_2^{5+}$		25			*d*

[a] All ratios are for 25 °C. For the trihydroxo- and dihydroxo-bridged complexes the ratios refer to the first bridge-cleavage reaction. [b] Only k_H and an upper limit for k_0 have been determined. [c] Only k_0 and an upper limit for k_H have been determined. [d] From the data in ref 16, interpreted on the basis of the mechanism presented in this work (see text). tacn = 9-aneN_3 = nane = 1,4,7-triazacyclononane.

but the postulated intermediate has never been observed. The acid-catalyzed path contributes significantly to the cleavage of the Δ,Λ-$(H_2O)(en)_2Rh(OH)Rh(en)_2(H_2O)^{5+}$ ion, for which $k_H/k_0 \approx 10$ at 25 °C. From Table III it is seen that the ratio k_H/k_0 increases as the number of hydroxo bridges increases. This trend could be the result of a kinetic effect (i.e., variations in the kinetic stability of the aqua-bridged species relative to that of the corresponding hydroxo-bridged species) or a thermodynamic effect (variations in the acid strength of the aqua-bridged intermediates). It is also seen that for monohydroxo- and dihydroxo-bridged species, respectively, there is an increasing contribution from an acid-catalyzed path in the sequence Cr(III) << Rh(III) ≈ Ir(III) ≈ Co(III) and that this follows the order that would be expected if the variations were due to a thermodynamic effect: cf. the variations of the acid strength of the mononuclear aqua complexes.[13,21,22]

The rate constant for the uncatalyzed bridge cleavage of the aqua–hydroxo ion Δ,Λ-$(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)^{4+}$ is about 10 times smaller at 25 °C than that for the cleavage of the diaqua ion Δ,Λ-$(H_2O)(en)_2Rh(OH)Rh(en)_2(H_2O)^{5+}$. The enhanced kinetic stability of the aqua–hydroxo ion is entirely due to a change in $\Delta S^{\ddagger}$ (Table I). However, since the charges of the reacting species are different, it is difficult to interpret this difference in $\Delta S^{\ddagger}$ in terms of e.g. transition-state structures. It is interesting, however, that the difference in reactivity parallels the difference in thermodynamic stabilities of the species (see also below). As discussed previously, the increased thermodynamic stability of the aqua–hydroxo ion can be rationalized on the basis of formation of an intramolecular hydrogen bond between the terminally bound water and hydroxide ligands (structure VI in Scheme II).[9-14] The formation of such hydrogen-bond-stabilized conformations in solution has been established for a number of rhodium(III), iridium(III), and chromium(III) hydroxo-bridged species and has recently also been established in the solid state[14] by an X-ray crystal-structure analysis. The kinetic impact of this hydrogen-bond interaction depends on the nature of the transition-state structure, i.e. whether the hydrogen bond is retained or is broken in the transition state, as shown schematically in Scheme II. Cleavage of the hydrogen bond prior to the formation of the transition state would offer a good explanation for the increased kinetic stability of this species. It should be noted, however, that factors other than hydrogen-bond interactions might influence the rate of hydroxo-bridge cleavage: charge effects are likely to increase the reactivity of the 5+ diaqua ion relative to that of the 4+ aqua-hydroxo ion, whereas the hydroxide ligand in the latter species might have a labilizing effect upon the hydroxo bridge. With these reservations in mind, we conclude that the results may be interpreted in terms of a non-hydrogen-bonded transition-state structure (II in Scheme II), rather than a hydrogen-bonded transition-state structure (V).

Scheme II[a]



[a] Stabilization of dinuclear species by intramolecular hydrogen-bond formation (VI) is well-established in the present and related systems. Stabilization of the mononuclear species by intermolecular hydrogen bonds (IV) is probably insignificant in the present system but may be important in other systems. Interconversion between mononuclear and dinuclear species may occur via non-hydrogen-bonded and hydrogen-bonded transition states, respectively, as schematically shown in II and V. Hydrogen bonds are shown by hyphens (- - -) and bond making and bond breaking by dots (···).

A kinetic study of the cleavage of the *trans*-$(H_2O)(tacn)Rh(OH)_2Rh(tacn)(H_2O)^{4+}$ ion to $Rh(tacn)(H_2O)_3^{3+}$ has recently been reported (tacn = 1,4,7-triazacyclononane, sometimes referred to as 9-aneN_3 or nane ligand).[16] Only one stage was observed, and for the [H^+] region 0.1 ≤ [H^+] ≤ 1.0 M a rate expression of the form $k_{obsd} = a + b[H^+]$ was observed. There are several different reaction schemes (within the framework of Scheme I) that would give rise to a rate expression of this form. It should be noted, however, that for [H^+] > 0.1 M in the case of the ethylenediamine system, eq 1 gives an approximate rate expression of the observed form; i.e., $k_{obsd} = k_4 + (k_3/K_{a3})[H^+]$. It seems likely that the same approximation may be valid for the tacn system, giving the values $k_4 = 1.4 \times 10^{-6}$ s^{-1} and $k_3/K_{a3} = 3.4 \times 10^{-5}$ s^{-1} M^{-1} at 25.0 °C. The fact that these values are similar to those found for the ethylenediamine system discussed here supports the validity of this approximation.

The condensation of *cis*-$Rh(en)_2(H_2O)(OH)^{2+}$ leads to the formation of monohydroxo- and dihydroxo-bridged species. It seems most likely that, in addition to the known meso isomers, the as yet uncharacterized racemic isomers are also formed, so that K_D is therefore a composite term. Assuming that the meso and racemic isomers are of equal thermodynamic stability, it can be shown[24] that $K_5 = k_5/k_{-5} = 2/K_D = 0.038$ (3) M (at 25.0 °C); $\Delta H°(K_5) = 14$ (2) kJ mol^{-1}, and $\Delta S°(K_5) = 21$ (6) J mol^{-1} K^{-1}. When this value is combined with the relevant, known acid-dissociation constants, also $K_4 = k_4/k_{-4}$ and K_6 = [*cis*-$Rh(en)_2$-

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(24) The gross equilibrium constant K_D is expressed in terms of true equilibrium constants by $K_D = (1 + K_1)/K_1K_5 + (1 + K_1')/K_1'K_5'$, in which K_1' and K_5' refer to the racemic isomers and are defined similarly to $K_1 = k_1/k_{-1}$ and $K_5 = k_5/k_{-5}$ (Scheme I). The assumption that the meso and the racemic isomers are equally stable, i.e., $K_1 \approx K_1'$ and $K_5 \approx K_5'$ leads to $K_5 \approx 2(1 + K_1)/K_1K_D \approx 2/K_D = 0.038$ (3) M. Combination of the value for K_5 with the known[13] acid dissociation constants of Δ,Λ-$(H_2O)(en)_2Rh(OH)Rh(en)_2(H_2O)^{5+}$ (K_{ai}^{d}) and of *cis*-$Rh(en)_2$-$(H_2O)_2^{3+}$ (K_{ai}^{m}) gives $K_4 = K_{a1}^{d}K_5/K_{a1}^{m}$ and $K_6 = K_5K_{a2}^{m}/K_{a2}^{d}$.

Table IV. Kinetic Data for Condensation Reactions

	k/M^{-1} s^{-1}	
reactants	M = *cis*-$Cr(H_2O)_4$[a]	M = *cis*-$Rh(en)_2$[b]
$M(OH_2)_2^{3+} + M(OH_2)_2^{3+}$		5×10^{-14}
$M(OH_2)(OH)^{2+} + M(OH_2)_2^{3+}$	6×10^{-6}	1×10^{-8}
$M(OH_2)(OH)^{2+} + M(OH_2)(OH)^{2+}$	$2.0\ (4) \times 10^{-4}$	6×10^{-6}
$M(OH)_2^{+} + M(OH_2)(OH)^{2+}$	$4\ (1) \times 10^{-2}$	
$M(OH)_2^{+} + M(OH)_2^{+}$	1.8 (2)	

[a] From ref 27. The 1+ and 2+ charged species probably have cis configurations. [b] This work. The values correspond to k_{-3}, k_{-4}, and k_{-5}, respectively, in Scheme I.

$(H_2O)(OH)^{4+}$][*cis*-$Rh(en)_2(OH)_2^{+}$]/[Δ,Λ-$(OH)(en)_2Rh(OH)$-$Rh(en)_2(OH)^{3+}$] may be calculated:[24] $K_4 = 3.5 \times 10^2$ M and $K_6 = 0.29$ M at 25.0 °C. The relative magnitude of the equilibrium constants is $K_4 >> K_6 > K_5$, which differs from the order $K_4 > K_5 > K_6$ expected on the basis of purely electrostatic considerations. The increased stability of the aqua–hydroxo ion is explicable on the basis of intramolecular hydrogen-bond formation between terminally coordinated water and hydroxide, as discussed above. For the related chromium(III) complex $(H_2O)_5Cr(OH)Cr(H_2O)_4(OH)^{4+}$, a value of $K_5 \approx 0.01$ M has been found,[25,26] which is comparable to the present value for rhodium(III).

From the kinetic data for the cleavage reactions and the related equilibrium constants the second-order rate constants for the condensation reactions can be estimated from the relations $k_{-3} = (k_3/K_{a3})(K_{a1}{}^{m}/K_4)$, $k_{-4} = k_4/K_4$, and $k_{-5} = k_5/K_5$. This gives the values that are listed in Table IV together with the corresponding values for the condensation of aquachromium(III) ions.[27] For both metal ions it is seen that the rate constants decrease by a factor of approximately 10^2 each time the charge of a reactant is lowered by one unit—the only exception being the rate constant k_{-3}, which is 10^5 times smaller than k_{-4}. This significantly reduced reactivity of two *cis*-$Rh(en)_2(H_2O)_2^{3+}$ ions with respect to condensation probably reflects the fact that the nucleophile in this case is a coordinated water ligand, whereas in the other reactions it can be a coordinated hydroxide ligand. Alternatively, the enhanced reactivity of the latter species may be the result of the labilizing effect of coordinated hydroxide.

In this context it is relevant that Ardon and Bino[28-30] have proposed that mononuclear aqua–hydroxo ions "dimerize" in aqueous solution, forming intermolecular hydrogen-bonded cation pairs as shown in Scheme II. The formation of such cation pairs in the solid state has been established by a number of X-ray crystal structure determinations. However, evidence for the formation in solution of such cation pairs has been reported only for the *cis*-$Cr(bpy)_2(H_2O)(OH)^{2+}$ ion (bpy = bipyridine), for which the ion-pair formation constant K_{ip} is 1.0 M^{-1} (K_{ip} = [IV]/[I]^2 in Scheme II).[28,30] In the present rhodium(III) system it is found that the ratio [dinuclear]/[mononuclear]^2 is constant for a large concentration range, providing indirect evidence that K_{ip} is negligible for this system, as is also found for the chromium(III) system[25,26] (a large K_{ip} value would require that the ratio [dinuclear]/[mononuclear] become constant).

As pointed out by Ardon and Bino, the observation[5] that *cis*-$Cr(C_2O_4)_2(H_2O)(OH)^{2-}$ condenses to give $(C_2O_4)_2Cr(OH)_2Cr(C_2O_4)^{4-}$ at a rate that becomes independent of the complex concentration at high concentration of the mononuclear species can be rationalized in terms of cation-pair formation, with the proviso that K_{ip} is large in this case. They also propose that this type of cation pair, even when formed in low concentration, could be the reactive species in the condensation reaction. If cation pairs were the reactive species, one would expect the transition-state structure V shown in Scheme II, rather than the non-hydrogen-bonded structure II. However, in the present rhodium(III) system the latter transition-state structure seems to be more in keeping with the kinetic data for the cleavage reaction, as mentioned above.

Conclusion

The condensation of *cis*-$Rh(en)_2(H_2O)_2^{3+}$ to give Δ,Λ-$(en)_2Rh(OH)_2Rh(en)_2^{4+}$ and the cleavage of the latter in acidic solution have been interpreted in terms of the equilibria given in Scheme I, the kinetic and thermodynamic parameters for which have now all been determined. The equilibration reactions between the monohydroxo- and dihydroxo-bridged species are orders of magnitude faster than those between the monohydroxo-bridged and mononuclear species, and both involve uncatalyzed and acid-catalyzed bridge-cleavage reactions. The latter are proposed to involve formation of a labile aqua-bridged intermediate, which is a very strong acid. An important feature is the fact that intramolecular hydrogen-bond formation stabilizes the species Δ,Λ-$(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)^{4+}$ and this has a significant thermodynamic and kinetic impact (e.g. a large $K_{a1}{}^{d}$ value and a small k_4 value), as discussed in this paper and in our previous studies of this (and related) systems. Stabilization in aqueous solution of the mononuclear aqua–hydroxo species by intermolecular hydrogen-bond interactions has been reported for related systems but appears to be of minor importance in the present system. It seems likely that the present results for rhodium(III) may serve in both a qualitative and a semiquantitative manner as a guideline for studies of related systems of aquarhodium(III) and other aquametal ions.

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Registry No. Δ,Λ-$(H_2O)(en)_2Rh(OH)Rh(en)_2(H_2O)^{5+}$, 83082-97-7; Δ,Λ-$(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)^{4+}$, 106017-59-8; *cis*-$Rh(en)_2(H_2O)(OH)^{2+}$, 53368-50-6; *cis*-[$Rh(en)_2(H_2O)(OH)$]$(ClO_4)_2$, 72709-24-1; *cis*-$Rh(en)_2(H_2O)_2^{3+}$, 41188-56-1.

Supplementary Material Available: A listing of observed and calculated rate constants (1 page). Ordering information is given on any current masthead page.

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