Contribution from the Chemistry Department, Royal Veterinary and Agricultural University,
Thorvaldsensvej 40, DK-1871 Frederiksberg C., Denmark

Formation of Racemic and Meso Isomers of Mono- and Dihydroxo-Bridged Dinuclear Ions by Hydrolysis of the *cis*-Aquahydroxobis(1,2-ethanediamine)rhodium(III) Ion

Morten J. Bjerrum, Karen Kaas, Erik Larsen,* Bente Nielsen, and Johan Springborg*,†

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The hydrolysis of racemic *cis*-$Rh(en)_2(H_2O)(OH)^{2+}$ in 1 M $NaClO_4$ at 60, 80, and 100 °C has been studied by HPLC, and it is shown that the equilibrium solutions contain the meso (Δ,Λ) and the racemic ($\Delta,\Delta/\Lambda,\Lambda$) isomers of the species $(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)^{4+}$ and $(en)_2Rh(OH)_2Rh(en)_2{}^{4+}$ together with the mononuclear species (Scheme I). Only the meso isomers of the dinuclear species have previously been isolated and characterized. In the present study, stable crystals of the racemic salts have been isolated viz. $\Delta,\Delta/\Lambda,\Lambda$-$[(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)](ClO_4)_4{\cdot}H_2O$ and $\Delta,\Delta/\Lambda,\Lambda$-$[(en)_2Rh(OH)_2Rh(en)_2](ClO_4)_4$. The equilibrium constant $K_{\text{isom}}(\text{M}) = [\Delta,\Delta\text{-}(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)^{4+}]/[\Delta,\Lambda\text{-}(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)^{4+}]$ has been determined by quantitative HPLC studies of equilibrium solutions: $K_{\text{isom}}(\text{M}) = 0.32\ (7)$ at 25 °C, $\Delta H^\circ = 0\ (4)$ kJ mol^{-1} and $\Delta S^\circ = -11\ (10)$ J mol^{-1} K^{-1}. On the basis of the values of $K_{\text{isom}}(\text{M})$ and previously published thermodynamic data for the dimerization of *cis*-$Rh(en)_2(H_2O)(OH)^{2+}$ it has been possible to calculate the equilibrium constants as well as ΔH° and ΔS° for the formation of each of the three diastereoisomers (Δ,Λ, Δ,Δ, and Λ,Λ) of $(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)^{4+}$ from racemic *cis*-$Rh(en)_2(H_2O)(OH)^{2+}$. The thermodynamics and kinetics of the equilibration reaction between the mono- and dihydroxo-bridged racemic species have been studied spectrophotometrically (1 M $NaClO_4$, 25-60 °C), and the constants K_1, k_1, and k_{-1} (Scheme I) have been determined.

Hydrolysis of aqua metal ions to form hydroxo-bridged polynuclear complexes has been reported for most transition metals and is of great significance in the aqueous chemistry of such ions.[1,2] The formation of hydroxo-bridged polynuclear complexes is thus related to precipitation and dissolution processes of hydroxides and oxides of relevance to geology. The polynuclear complexes are also found to be of relevance to biology, for example in providing two-electron-redox reagents occurring in certain enzymes.[3]

In spite of the wide occurrence of these complexes, studies of their thermodynamic and kinetic properties have been rather fragmentary: systematic studies have been carried out only for a few series of robust dinuclear complexes, mainly of chromium(III), rhodium(III), and cobalt(III). Studies of the equilibria between the mono- and dihydroxo-bridged dinuclear species and between the di- and trihydroxo-bridged dinuclear species have been reported for a number of complexes of the above-mentioned metals.[4] While these intramolecular bridge-formation (and bridge-cleavage) processes now seem to be rather well understood, the corresponding intermolecular reactions have been studied only in a few cases.[1,4] Equilibrium studies of the dimerization process given by eq 1 have been reported for many metal aqua ions, but

$$ML_n(OH)^{(z-1)+} + ML_n(OH_2)^{z+} \rightleftarrows L_nM(OH)ML_n{}^{(2z-1)+} + H_2O \quad (1)$$

very few kinetic studies of these systems have been reported. In the case of aqua ions (L = H_2O), the studies are complicated by the fact that well-defined crystalline salts of monohydroxo-bridged dinuclear species have never been obtained, and therefore the structures of these species are in many cases not known with certainty. In many respects, the ammine and amine complexes mentioned above are more obvious candidates for studies in this field. Various polynuclear species have been isolated in well-defined crystalline form and characterized by single-crystal X-ray structure analysis.[4] The blocking of ligand sites with substitutionally inert N ligands greatly reduces the number of possible bridging skeletons of the polynuclear species. The use of polydentate amine ligands has, however, a serious drawback: the number of possible isomers may be quite large owing to the possibility of different configurations of the chelate ring systems. This aspect and the solution to the imposed problems relevant to the bis(1,2-ethanediamine)rhodium(III) system are the subject of the present work.

It was shown previously that *cis*-$Rh(en)_2(H_2O)(OH)^{2+}$ dimerizes in aqueous solution to form mono- and dihydroxo-bridged species.[5] As shown in Figure 1, the dinuclear species may occur in three diastereoisomeric forms: a racemic pair, Δ,Δ and Λ,Λ, and a meso isomer, Δ,Λ. The gross equilibrium constant K_D = [dinuclear]/[*cis*-$Rh(en)_2(H_2O)(OH)^{2+}]^2$ has previously been determined spectrophotometrically (see eq 7 below). Only for the meso isomers of the dinuclear species has an isolation followed by an identification been reported previously: Heating of solid *cis*-$[Rh(en)_2(H_2O)(OH)]S_2O_6$ yields stereospecifically Δ,Λ-$[(en)_2Rh(OH)_2Rh(en)_2](S_2O_6)_2$.[6,7] Hydrolysis of this compound yields the corresponding monohydroxo-bridged species, which has been isolated as a perchlorate salt, Δ,Λ-$[(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)](ClO_4)_4$.[8]

Kinetic and thermodynamic studies of the equilibrium between the mono- and dihydroxo-bridged Δ,Λ-isomers have been reported,[8] as have the kinetics for the cleavage of Δ,Λ-$(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)^{4+}$ (and of its protonated diaqua form) into mononuclear species.[5] These studies revealed that both uncatalyzed and acid-catalyzed bridge-cleavage and bridge-formation reactions take place. The acid-dependent path contributes significantly only at $[H^+] \geq 10^{-4}$ and therefore has not been included in Scheme I.

The equilibrium constant K_D is a composite term that may be expressed by the equilibrium constants shown in Scheme I. We have previously determined one of these constants, viz. K_1 (Δ,Λ) (see Scheme I). At that time it was not possible to determine the other constants in Scheme I, since the racemic isomers were uncharacterized. However, by assuming that the meso and racemic isomers were equally stable, a rough estimate of the formation constants of the monohydroxo-bridged species could be calculated from the values of K_D and $K_1(\Delta,\Lambda)$.[5]

The suggestion that hydrolysis of racemic *cis*-$Rh(en)_2(H_2O)(OH)^{2+}$ affords the meso and racemic dinuclear species in equal amounts clearly indicated a synthetic route for the new racemic species. In the present work we have followed this line and have, assisted by the analytical advances offered by HPLC, succeeded in preparing pure and stable salts of the racemic isomer

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* To whom correspondence should be addressed.

† Present address: New Mexico State University, Department of Chemistry, Box 30001, Dept. 3C, Las Cruces, NM 88003-0001.

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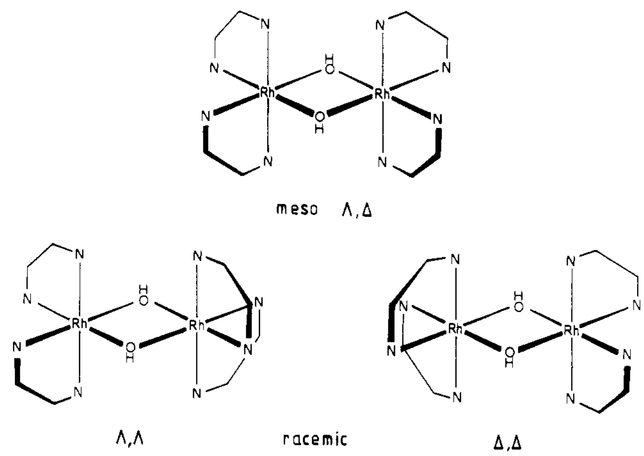
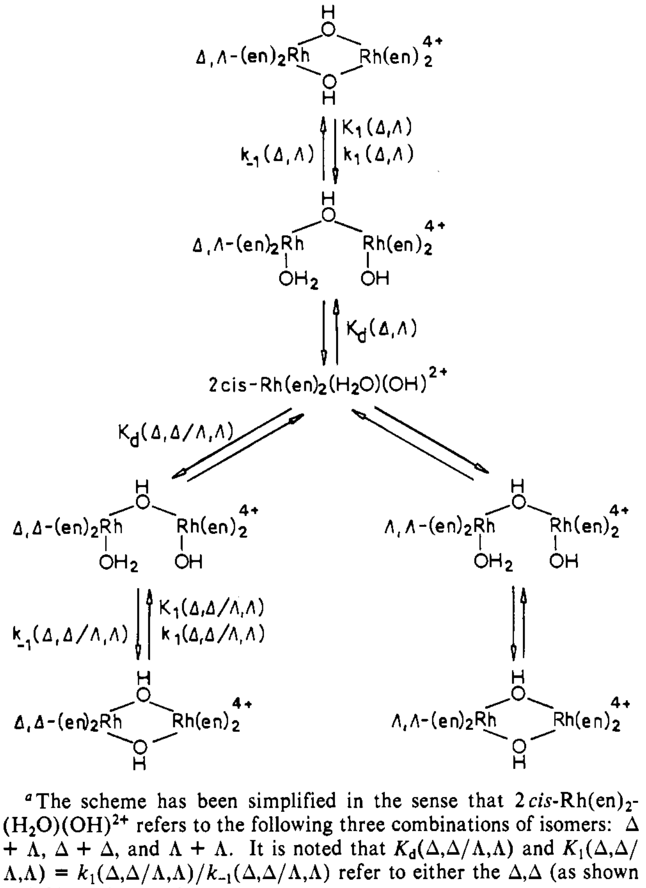


Figure 1. Isomers of the $(en)_2Rh(OH)_2Rh(en)_2^{4+}$ species studied in the present work.

Scheme I. Equilibria Studied in This and Previous[5,8] Work[a]



[a] The scheme has been simplified in the sense that 2*cis*-$Rh(en)_2(H_2O)(OH)^{2+}$ refers to the following three combinations of isomers: Δ + Λ, Δ + Δ, and Λ + Λ. It is noted that K_d(Δ,Δ/Λ,Λ) and K_1(Δ,Δ/Λ,Λ) = k_1(Δ,Δ/Λ,Λ)/k_{-1}(Δ,Δ/Λ,Λ) refer to either the Δ,Δ (as shown at left) or the Λ,Λ isomers.

of the dinuclear species with one or two hydroxo bridges. This achievement finally made it possible to determine accurately the remaining equilibrium constants in Scheme I.

Experimental Section

Materials and Instruments. The complexes Δ,Λ-$[(en)_2Rh(OH)_2Rh(en)_2](ClO_4)_4$ and *cis*-$[Rh(en)_2(OH)(H_2O)](ClO_4)_2$ were synthesized as described previously.[5,8] All reagents were of analytical grade. CO_2-free deionized water was used for all solutions. Absorption spectra were measured on a Perkin-Elmer Lambda diode array spectrophotometer. Ion-exchange high-performance liquid chromatography was performed on Waters HPLC equipment, as described previously.[9] C, H, N and Cl analyses were performed at the Microanalytical Laboratory at the H.C. Ørsted Institute, Copenhagen.

Table I. Constants Used for the Determination of the Isomerization Constants and Dimerization Constants Given in Table II[a]

T/°C	K_1(Δ,Λ)[b]	K_1(Δ,Δ/Λ,Λ)[c]	K_D[d]	K_{RM}[e]
100	3.6 (3)	0.95 (8)	22.9 (7)	0.75 (4)
80	4.6 (3)	1.11 (7)	31.1 (9)	0.66 (2)
60	6.2 (2)	1.32 (5)	39.7 (33)	0.69 (3)
25	11.2 (3)	1.89 (4)		

[a] The standard deviations in this and the following tables have been calculated by using standard procedures and are given in parentheses: 12.0 (2) means that the value 12.0 has been determined with a standard deviation of 0.2. Likewise 39.7 (33) means that the standard deviation is 3.3. [b] Calculated from the original data of ref 8. In this reference the error in K^{25}_1 (Δ,Λ) = 11.2 has been given as 0.5, but it should be 0.3. $\Delta S°$ was quoted to be −28 (8), but should be −27 (4) J mol^{-1} K^{-1}. [c] This work; see Table IV. [d] From ref 5, but corrected as described in the text. [e] This work. Determined by HPLC as described in the text.

Preparations. *Caution!* The solid complex salts described below may *detonate* violently when subjected to mechanical shock. They must therefore be handled with caution and should not be prepared in quantities larger than those described here.

1. Δ,Δ/Λ,Λ-(μ-Hydroxo)[aquabis(1,2-ethanediamine)rhodium(III)]-bis(1,2-ethanediamine)hydroxorhodium(III) Perchlorate Monohydrate, Δ,Δ/Λ,Λ-$[(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)](ClO_4)_4\cdot H_2O$. A solution of *cis*-$[Rh(en)_2(H_2O)(OH)](ClO_4)_2$ (2.0 g, 4.38 mmol) in water (5 mL) was heated (in an ampule or under reflux) to 100 °C for 80 min. The solution was cooled to 25 °C, and then 2.00 M $HClO_4$ (2.50 mL) was added. After 60 s, the solution was cooled in ice, and then 2.00 M NaOH (2.50 mL) and a saturated solution of $NaClO_4$ (5 mL) were added in that order. Cooling in ice was continued for 1 h, and yellow crystals separated. The crystals were filtered off, washed with 96% ethanol, and dried in the air. The crude product (1.24 g) was dissolved in ice-cold water (11 mL) and the pH was adjusted to approximately 4 by dropwise addition of 1 M $HClO_4$ (approximately 0.4 mL). A saturated solution of $NaClO_4$ (5.5 mL) was then added, and cooling was continued for 15 min. The precipitate was isolated as above. This product (0.63 g) was dissolved in ice-cold water (8.2 mL) and reprecipitated by addition of a saturated solution of $NaClO_4$ (1.9 mL). The precipitate was isolated as above (yield 0.57 g). Recrystallization once more in the same way gave a pure sample of Δ,Δ/Λ,Λ-$[(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)](ClO_4)_4\cdot H_2O$. Yield: 0.49 g [25% based upon *cis*-$[Rh(en)_2(H_2O)(OH)](ClO_4)_2$]. Anal. Calcd for $Rh_2C_8H_{38}N_8Cl_4O_{20}$: C, 10.51; H, 4.19; N, 12.26; Cl, 15.51. Found: C, 10.45; H, 4.10; N, 12.29; Cl, 15.45. The purity was further tested by HPLC as described in the Results section. Spectral data are given in Table III.

2. Δ,Δ/Λ,Λ-Bis(μ-hydroxo)bis[bis(ethylenediamine)rhodium(III)] Perchlorate, Δ,Δ/Λ,Λ-$[(en)_2Rh(OH)_2Rh(en)_2](ClO_4)_4$. This compound was made by heating 100–200 mg of pure Δ,Δ/Λ,Λ-$[(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)](ClO_4)_4\cdot H_2O$ for 70 h at 140 °C. Anal. Calcd for $Rh_2C_8H_{34}N_8Cl_4O_{18}$: C, 10.94; H, 3.90; N, 12.76; Cl, 16.15. Found: C, 10.58; H, 3.83; N, 12.53; Cl, 16.18. The purity was tested by HPLC as described in the Results section. Spectral data are given in Table III.

Spectroscopic Measurements. The spectra of 1 M $NaClO_4$ solutions (pH ~ 6) of Δ,Δ/Λ,Λ-$[(en)_2Rh(OH)_2Rh(en)_2](ClO_4)_4$ and Δ,Δ/Λ,Λ-$[(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)](ClO_4)_4\cdot H_2O$ were measured in the wavelength region 190–400 nm at 25, 40, and 60 °C. The spectra changed with time and became constant after about 90, 24, and 3 min, respectively. The change of the absorbance with time followed the expression $A = A_\infty + (A_0 - A_\infty)\exp(-k_{obs}t)$, as shown by nonlinear least-square calculations. A_0 is the absorbance at $t = 0$, A_∞ is the absorbance at completion (equilibrium), and k_{obs} is the observed pseudo-first-order rate constant for the reaction. The calculations were made by using 211 wavelengths in the region 190–400 nm.

From the spectra of the pure monohydroxo-bridged species [ϵ_0(M)] and the pure dihydroxo-bridged species [ϵ_0(D)] and the spectra at completion [ϵ_∞], the equilibrium constant K_1(Δ,Δ/Λ,Λ) in Scheme I was calculated by using eq 2, where ϵ^λ are the molar absorbances measured for 141 wavelengths, λ, in the region 260–400 nm.

$$\epsilon_\infty{}^\lambda = \frac{[\epsilon_0{}^\lambda(M)]K_1 + \epsilon_0{}^\lambda(D)}{1 + K_1} \qquad (2)$$

The values of k_{obs} were identical for solutions initially containing the monohydroxo-bridged species or the dihydroxo-bridged species. Using values of K_1(Δ,Δ/Λ,Λ) determined above, and the relations $k_{obs} = k_1$(Δ,Δ/Λ,Λ) + k_{-1}(Δ,Δ/Λ,Λ) and K_1(Δ,Δ/Λ,Λ) = k_1(Δ,Δ/Λ,Λ)/k_{-1}(Δ,Δ/Λ,Λ), values of k_1(Δ,Δ/Λ,Λ) and k_{-1}(Δ,Δ/Λ,Λ) were then calculated. The activation parameters were then calculated by using the relation k

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Table II. Thermodynamic Data for the Isomerization and the Dimerization Reactions in 1 M $NaClO_4$

constant	K^{25}	K^{60}	K^{80}	K^{100}	$\Delta H°$/kJ mol^{-1}	$\Delta S°$/J mol^{-1} K^{-1}
$K_{isom}(M)$	0.32 (7)	0.31 (2)	0.31 (2)	0.31 (3)	−0.5 (36)	−11 (10)
$K_{isom}(D)$	1.9 (5)	1.5 (1)	1.3 (1)	1.2 (2)	−6 (4)	−15 (12)
$K_d(\Delta,\Lambda)/M^{-1}$	143 (27)	71 (5)	50 (3)	37 (3)	−17 (3)	−14 (9)
$K_d(\Delta,\Delta/\Lambda,\Lambda)/M^{-1}$	46 (4)	22 (1)	16 (1)	12 (1)	−17 (3)	−25 (4)

[a] The $\Delta H°$ and $\Delta S°$ values have been obtained by least-square calculations using the data in Table I, and from these parameters the values of the equilibrium constants at 25–100 °C have been calculated.

Table III. Ligand-Field Spectra of the Dinuclear Species at 25 °C[a]

cations	ϵ_{max}; λ_{max} Δ,Λ-isomers[b]		$\Delta,\Delta/\Lambda,\Lambda$-isomers[c]	
$(H_2O)(en)_2Rh(OH)Rh(en)_2(H_2O)^{5+}$	590; 329	553; 273	642; 333[d]	587; 276[d]
$(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)^{4+}$	514; 330	553; 270 (sh)	524; 333[e]	564; 273[e] (sh)
$(HO)(en)_2Rh(OH)Rh(en)_2(OH)^{3+}$	519; 337	635; 278	583; 338[f]	711; 283[f]
$(en)_2Rh(OH)_2Rh(en)_2{}^{4+}$	535; 331		446; 333[g]	

[a] All data have been obtained by extrapolation back to the time of dissolution. The molar absorption coefficient ϵ is given in L mol^{-1} cm^{-1}, and the wavelength λ is given in nm. [b] From ref 8. [c] This work. [d] Identical values were obtained for $\Delta,\Delta/\Lambda,\Lambda$-$[(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)](ClO_4)_4 \cdot H_2O$ in 1 M $HClO_4$ and in 0.1 M $HClO_4$, 0.9 M $NaClO_4$. [e] $\Delta,\Delta/\Lambda,\Lambda$-$[(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)](ClO_4)_4 \cdot H_2O$ in 1 M $NaClO_4$. [f] Identical values were obtained, for $\Delta,\Delta/\Lambda,\Lambda$-$[(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)](ClO_4)_4 \cdot H_2O$ in 0.01 M NaOH, 1 M $NaClO_4$ and in 0.05 M NaOH, 0.95 M $NaClO_4$. [g] Identical values were obtained for $\Delta,\Delta/\Lambda,\Lambda$-$[(en)_2Rh(OH)_2Rh(en)_2](ClO_4)_4$ in 1 M $NaClO_4$ (25 °C) and in 1 M $HClO_4$ (1.0 °C).

$= (k_BT/h) \exp(\Delta S^\ddagger/R - \Delta H^\ddagger/RT)$.

Preparation of Equilibrium Solutions. Solutions containing mononuclear and dinuclear species in equilibrium were made as described previously (see also Results).[5] The heated solutions were quenched by cooling to 0 °C and were normally analyzed within 2 days. Solutions kept for longer periods were frozen and stored at −20 °C.

HPLC Measurements. A TSK gel SP-5PW column from Toyo Soda, Japan, with length 75 mm and inner diameter 7.5 mm was used in all experiments. Solutions to be analyzed, and the eluent, were filtered through a Millex HV_4 filter unit (Durapore 0.45 μm) prior to injection. In all experiments the eluent was 0.22 M Na_2SO_4. The flow-rate was 1 mL min^{-1} and the pressure approximately 350 psi. The absorbance of the eluate at 300 nm was recorded, typically by using an absorbance region of 0–0.01. The chromatography was performed at 0 or 25 °C. At 25 °C, the column was kept at 25.0 ± 0.1 °C with a thermostated water bath, while the other parts of the instrument were at ambient temperature. At 0 °C, the column as well as the wire from the inlet to the column were kept at 0 °C by using an ice bath. Chromatography at 0 °C was carried out when it was essential to prevent equilibration between the mono- and dihydroxo-bridged species during the analysis. The half-lives of this reaction for the meso and the racemic isomers are 23 and 14 min, respectively, at 25 °C, and 9 and 5 h, respectively, at 0 °C (see Results). The time elapsing from the dissolution of the sample to the time when it is bound to the column is about 1 min.

The ratio between the concentrations of two species, C_1/C_2, was determined from the HPLC curves using eq 3, in which A_1 and A_2 are the

$$C_1/C_2 = A_1\epsilon_2/A_2\epsilon_1 \qquad (3)$$

peak areas obtained by integration of the elution curves for the two species and ϵ_1 and ϵ_2 are the molar absorbances of the two species at 300 nm.

Results

HPLC Studies of Equilibrium Solutions of Mono- and Dinuclear Species. Qualitative Results. The equilibrium between *cis*-$Rh(en)_2(H_2O)(OH)^{2+}$ and its corresponding dinuclear species in 1 M $NaClO_4$ was established at 60, 80, and 100 °C. Equilibrium solutions were made by heating solutions of racemic *cis*-$[Rh(en)_2(H_2O)(OH)](ClO_4)_2$ or of the meso dimer Δ,Λ-$[(en)_2Rh(OH)_2Rh(en)_2](ClO_4)_4$ for 70, 8, and 1 h, i.e. the same reaction times as used in our previous study of the same reaction.[5] These solutions represent equilibrium situations that were demonstrated previously by spectrophotometric measurements and by potentiometric pH measurements. In the present study this was further, and very strongly, supported, first by the fact that the HPLC curves did not change upon further heating and second by the observation (see Figure 2) that HPLC chromatograms for solutions initially containing either *cis*-$[Rh(en)_2(H_2O)(OH)](ClO_4)_2$ or Δ,Λ-$[(en)_2Rh(OH)_2Rh(en)_2](ClO_4)_4$, respectively, were identical. The total concentration of rhodium(III), C_{Rh} = [mononuclear] + 2[dinuclear], was varied from 10^{-3} to 1.0 M. Figure 3 shows how the HPLC curves for solutions equilibrated at 100.0 °C change when C_{Rh} is varied; similar changes were found for 60 and 80 °C. At large C_{Rh}, five dominant peaks were observed and the species identified as follows (in the order of decreasing elution rate): a, *cis*-$Rh(en)_2(H_2O)(OH)^{2+}$; b, $\Delta,\Delta/\Lambda,\Lambda$-$(en)_2Rh(OH)_2Rh(en)_2{}^{4+}$; c, Δ,Λ-$(en)_2Rh(OH)_2Rh(en)_2{}^{4+}$; d, Δ,Λ-$(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)^{4+}$; e, $\Delta,\Delta/\Lambda,\Lambda$-$(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)^{4+}$. The identification of a, c, and d

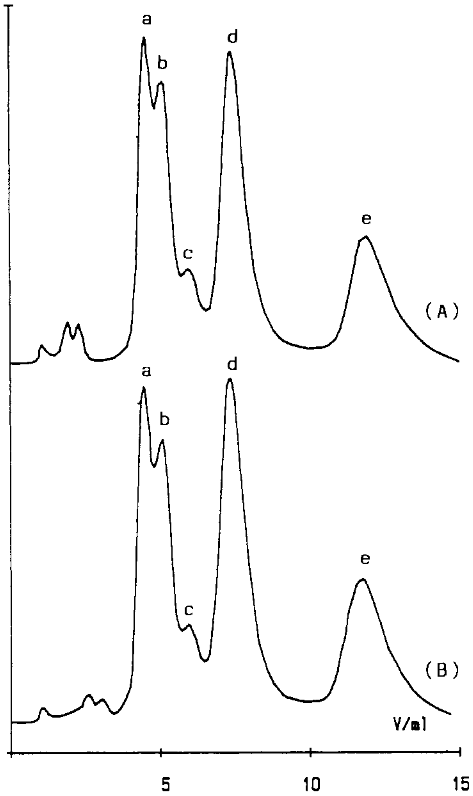

Figure 2. HPLC chromatograms (measured at 25 °C) for solutions made by heating a solution of either *cis*-$[Rh(en)_2(H_2O)(OH)](ClO_4)_2$ (A) or Δ,Λ-$[(en)_2Rh(OH)_2Rh(en)_2](ClO_4)_4$ (B) in 1 M $NaClO_4$ for 1 h at 100.0 °C. In both experiments, C_{Rh} = 0.22 M. Peaks a–e have been assigned as follows: (a) *cis*-$Rh(en)_2(H_2O)(OH)^{2+}$; (b) $\Delta,\Delta/\Lambda,\Lambda$-$Rh_2(\mu\text{-}OH)_2{}^{4+}$; (c) Δ,Λ-$Rh_2(\mu\text{-}OH)_2{}^{4+}$; (d) Δ,Λ-$Rh_2(\mu\text{-}OH)^{4+}$, (e) $\Delta,\Delta/\Lambda,\Lambda$-$Rh_2(\mu\text{-}OH)^{4+}$.

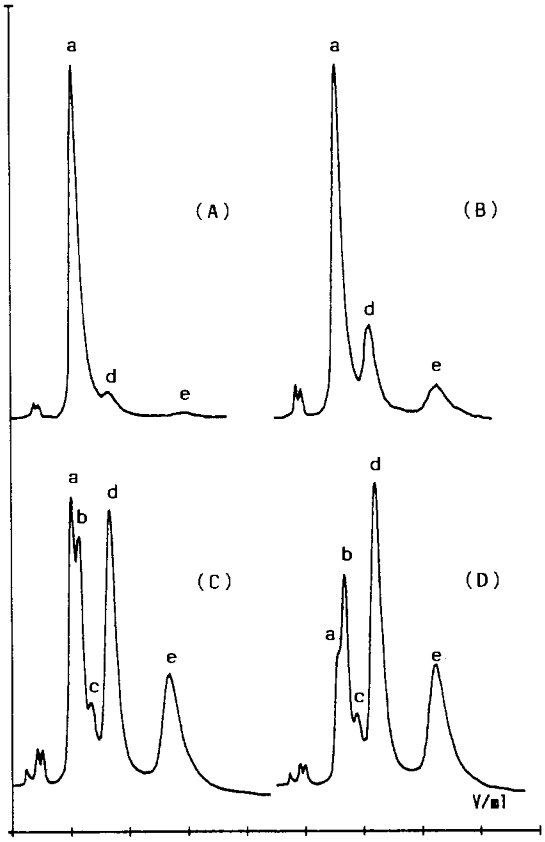

Figure 3. HPLC chromatograms (measured at 25 °C) for equilibrium solutions made at 100 °C and with C_{Rh} = 0.0023 (A), 0.022 (B), 0.22 (C), and 0.88 M (D). Assignments of the peaks a–e is as in Figure 2.

was made unambiguously by using samples of authentic salts for which the configuration is now well established. Identification of b and e as the new racemic isomers of the di- and monohydroxo-bridged species, respectively, was preliminarily based upon the expected similarity in behavior of the meso and racemic isomers (similar elution rates and similar ratios between mono- and dihydroxo-bridged species). On the basis of these observations, it was possible to design methods for the isolation of salts of the pure racemic isomers (see the following section), and the assignment of the five major peaks of the chromatograms was thereby considered unambiguous.

In addition to the five major peaks for species a–e, one to three peaks were always observed in HPLC curves for the equilibrium solution. These peaks appeared before peak a [*cis*-$Rh(en)_2(H_2O)(OH)^{2+}$], indicating low-charged species. In some experiments, the relative amounts of these species were found to increase with decreasing C_{Rh}, but this was not always the case. For $C_{Rh} \geq 2 \times 10^{-2}$ M the content of these products, as judged from the relative peak areas, was about 1%, while for $C_{Rh} = 10^{-3}$ M a content varying from 2 to 10% was observed. Although precautions were taken to avoid access of carbon dioxide to the stock solution, it seems likely that these byproducts are carbonato complexes. *cis*-$Rh(en)_2(OH)(H_2O)^{2+}$ has been reported[10] to react rapidly with carbon dioxide, and the presence of contamination by carbon dioxide in the 1 M $NaClO_4$ stock solutions would explain the observed increase in the relative yield of these byproducts with decreasing C_{Rh}.

Determination of the Equilibrium Constants K_{isom}(M), K_{isom}(D), K_d(Δ,Λ), and K_d(Δ,Δ/Λ,Λ). The HPLC analysis of the equilibrium solutions (60, 80, and 100 °C) was made at 25 °C. The solutions were kept for ca. 2 h at 25 °C prior to the measurements. During this time reequilibration takes place between the mono- and dihydroxo-bridged species for both the Δ,Λ and Δ,Δ/Λ,Λ configurations ($t_{1/2} \sim 20$ min), whereas reequilibration between meso and racemic isomers or between mono- and dinuclear species is negligible.

Figure 3 shows how the relative amounts of the dinuclear species increase as C_{Rh} increases, as expected from the equilibria shown in Scheme I. It is readily seen that the equilibrium constants defined in Scheme I [K_1(Δ,Λ), K_1(Δ,Δ/Λ,Λ), K_d(Δ,Λ), and K_d(Δ,Δ/Λ,Λ)] can, in principle, be determined from chromatograms like those shown in Figure 3. However, the relatively poor separation between the peaks for *cis*-$Rh(en)_2(H_2O)(OH)^{2+}$ and those for the isomers of $(en)_2Rh(OH)_2Rh(en)_2^{4+}$ hampered a direct determination of these constants. The peaks for the two monohydroxo-bridged species are well separated, and their ratio, K^t_{RM} = [racem]/[meso], can therefore be determined accurately; *t* refers to the temperature (in °C) at which the equilibration between the mono- and dinuclear species has been attained. K^t_{RM} is not an equilibrium constant, since the equilibrium solutions were reequilibrated and measured at 25 °C, as mentioned above. However, the true equilibrium constant K^t_{isom}(M) defined in eq 4 may be calculated from K^t_{RM} by using eq 5. The necessary values of K_1(Δ,Λ) and K_1(Δ,Δ/Λ,Λ) at the different temperatures shown in Table I have been calculated from the values of $\Delta H°$ and $\Delta S°$ previously reported[8] for K_1(Δ,Λ) and from those determined in this study for K_1(Δ,Δ/Λ,Λ) (see below). The values of K_{isom}(M) at 60, 80, and 100 °C obtained in this way then gave the $\Delta H°$ and $\Delta S°$ values shown in Table II. In Table II are also given the thermodynamic parameters for the corresponding isomerization of the dihydroxo-bridged species defined in eq 6,

$$\Delta,\Lambda\text{-}(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)^{4+} \underset{}{\overset{K_{\mathrm{isom}}(M)}{\rightleftharpoons}} \Delta,\Delta\text{-}(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)^{4+} \quad (4)$$

$$K^t_{\mathrm{isom}}(M) = \{{}^1\!/_2 K^t_{RM}[K^t_1(\Delta,\Delta/\Lambda\Lambda)][1 + K^t_1(\Delta,\Lambda)][1 + K^{25}_1(\Delta,\Delta/\Lambda\Lambda)]K^{25}_1(\Delta,\Lambda)\}/\{[K^t_1(\Delta,\Lambda)][1 + K^t_1(\Delta,\Delta/\Lambda,\Lambda)][1 + K^{25}_1(\Delta,\Lambda)]K^{25}_1(\Delta,\Delta/\Lambda\Lambda)\} \quad (5)$$

$$\Delta,\Lambda\text{-}(en)_2Rh(OH)_2Rh(en)_2^{4+} \overset{K_{\mathrm{isom}}(D)}{\rightleftharpoons} \Delta,\Delta\text{-}(en)_2Rh(OH)_2Rh(en)_2^{4+} \quad (6)$$

$K_{\mathrm{isom}}(D) = K_1(\Delta,\Lambda)\, K_{\mathrm{isom}}(M)/K_1(\Delta,\Delta/\Lambda,\Lambda)$. The dimerization constants K_d(Δ,Λ) and K_d(Δ,Δ/Λ,Λ) have been calculated from the present data in combination with our previously determined[5] values of the gross equilibrium constant K_D shown in eq 7. In

$$K_D = \frac{[\text{dinuclear}]}{[cis\text{-}Rh(en)_2(H_2O)(OH)^{2+}]^2} \quad (7)$$

eq 7, [dinuclear] is the sum of the concentrations of both meso and racemic isomers of $(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)^{4+}$ and $(en)_2Rh(OH)_2Rh(en)_2^{4+}$. K_D was previously determined by spectrophotometry and by titration. Although good agreement was obtained between the two methods, the values obtained by titration are estimated to be the most accurate and only these have been used for the present calculations. It is noted that the values of K_D listed in Table I differ from those given in ref 5, which is due to corrections as described here. The acid dissociation constants of Δ,Λ-$(H_2O)(en)_2Rh(OH)Rh(en)_2(H_2O)^{5+}$ at 25 °C are pK_{a1} = 2.372 (7) ($\Delta H°$ = 28 (4) kJ mol^{-1} and $\Delta S°$ = 49 (13) J mol^{-1} K^{-1})[8] and pK_{a2} = 9.128 (7) ($\Delta H°$ = 39.5 (6) kJ mol^{-1} and $\Delta S°$ = −42 (2) J mol^{-1} K^{-1}),[8,11] and preliminary experiments showed that the racemic isomers have similar values. The content of $(H_2O)(en)_2Rh(OH)Rh(en)_2(H_2O)^{5+}$ and $(HO)(en)_2Rh(OH)Rh(en)_2(OH)^{3+}$ will therefore be negligible in the equilibrium solutions, which have pH ≈ 7.3 (at 25 °C). However, the pK_a values for *cis*-$Rh(en)_2(H_2O)_2^{3+}$ are separated by only 1.9 units in p*K*, and the equilibrium solutions will therefore contain significant amounts of *cis*-$Rh(en)_2(H_2O)_2^{3+}$ (approximately 9%) and *cis*-$Rh(en)_2(OH)_2^{+}$ (approximately 9%). This was ignored in our preliminary estimate of K_D, but it has been included in the calculations of the new K_D values listed in Table I by using the following pK_a values for *cis*-$Rh(en)_2(H_2O)_2^{3+}$ (25 °C): pK_{a1} = 6.338 (2) ($\Delta H°$ = 43.2 (6) kJ mol^{-1} and $\Delta S°$ = 23 (2) J mol^{-1}

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[10] van Eldik, R. *Adv. Inorg. Bioinorg. Mech.* **1984**, *3*, 275.

K^{-1}) and $pK_{a2} = 8.244$ (2) ($\Delta H^\circ = 41.9$ (8) kJ mol^{-1} and $\Delta S^\circ = -17$ (3) J mol^{-1} K^{-1}).[8,11]

Values of $K_d(\Delta,\Lambda)$ and $K_d(\Delta,\Delta/\Lambda,\Lambda)$ at the three temperatures 60, 80, and 100 °C were then calculated by eq 8 and 9, respectively,

$$K_d(\Delta,\Lambda) = \frac{[\Delta,\Lambda\text{-}(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)^{4+}]}{[\Delta\text{-}cis\text{-}Rh(en)_2(H_2O)(OH)^{2+}][\Lambda\text{-}cis\text{-}Rh(en)_2(H_2O)(OH)^{2+}]} = 4K_D[K_1(\Delta,\Lambda)][K_1(\Delta,\Delta/\Lambda,\Lambda)]/\{[K_1(\Delta,\Delta/\Lambda,\Lambda)][1 + K_1(\Delta,\Lambda)] + [2K_{isom}(M)][K_1(\Delta,\Lambda)][1 + K_1(\Delta,\Delta/\Lambda,\Lambda)]\} \quad (8)$$

$$K_d(\Delta,\Delta/\Lambda\Lambda) = \frac{[\Delta,\Delta\text{-}(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)^{4+}]}{[\Delta\text{-}cis\text{-}Rh(en)_2(H_2O)(OH)^{2+}]^2} = [K_{isom}(M)]K_d(\Delta,\Lambda) \quad (9)$$

and from these values the thermodynamic parameters given in Table II were obtained. In the above calculations it has been assumed that all the equilibrium constants have been determined by using a salt medium with a constant ionic strength of 1.0 M, which, however, is not strictly true for the constant K_{RM}. Most of the determinations of K_{RM} have been made by using solutions initially containing 0.2 M *cis*-$[Rh(en)_2(H_2O)(OH)](ClO_4)_2$ in 1 M $NaClO_4$. The ionic strength of these solutions is about 1.9 M. However, for a series of equilibrium solutions (made at 100 °C) with C_{Rh} varying from 0.02 M ($I \approx 1.1$ M) to 0.9 M ($I \approx 5$ M), no variations in K_{RM} with the ionic strength were found. It is therefore concluded that the values of K_{RM} given in Table I are valid also for $I = 1.0$ M. In this context it is relevant that our previous determination of K_D, which undoubtedly is more sensitive than K_{RM} to variations in the ionic strength, was made by using a constant ionic strength, $I = 1.07$ M ($C_{Rh} = 2 \times 10^{-2}$ M in 1 M $NaClO_4$).[5]

Isolation of Salts of the Meso and Racemic Isomers. Equilibrium solutions were prepared at 100 °C as described above, starting with *cis*-$[Rh(en)_2(H_2O)(OH)](ClO_4)_2$.

In order to obtain a high content of dinuclear species, a large rhodium(III) concentration was used ($C_{Rh} = 0.88$ M). From the results given above (Table II; see also Figure 3), it is calculated that such solutions contain 17% of *cis*-$Rh(en)_2(H_2O)(OH)^{2+}$, 33% and 20% of the Δ,Λ and $\Delta,\Delta/\Lambda,\Lambda$ isomers, respectively, of $(H_2O)(en)_2Rh(OH)_2Rh(en)_2(OH)^{4+}$, and 9% and 21% of the Δ,Λ- and $\Delta,\Delta/\Lambda,\Lambda$-isomers, respectively, of $(en)_2Rh(OH)_2Rh(en)_2^{4+}$ [the percentages are given with respect to moles of rhodium(III)]. Since the meso and racemic isomers of the monohydroxo-bridged species were found in the HPLC studies to be well separated from the other species, it was clear that this technique provided a straightforward method for isolating the racemic species as a pure salt. However, with the ion-exchange columns available for the present study, it was only possible to load the column with very small amounts in each experiment, and this was considered to be an impractical method for the present purpose. Therefore, separation of the equilibrium mixture by crystallization was studied. Precipitation of the tetrachlorozincate salt gave no significant separation of the meso and racemic isomers. Precipitation of the trifluoromethanesulfonate and the dithionate salts, respectively, gave a significant enrichment in the Δ,Λ isomers. Precipitation of the nitrate salt followed by one reprecipitation gave a sample that was shown by HPLC analysis to contain 95% Δ,Λ-$(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)^{4+}$. Further purification of this salt was not attempted, since the Δ,Λ isomers can very easily be obtained in high yield by the solid-state dimerization reaction of *cis*-$[Rh(en)_2(H_2O)(OH)]S_2O_6$, as described previously.[6-8]

Finally it was found that precipitation of the perchlorate salt gave an almost pure sample of the monohydroxy-bridged $\Delta,\Delta/\Lambda,\Lambda$ isomer. In order to increase the yield of this species, and also to avoid contamination with the dihydroxo-bridged species, the equilibrium mixture was made acidic (pH ≈ 0) and kept at 25 °C for 60 s. During this time the dihydroxo-bridged species are converted quantitatively to the monohydroxo-bridged species, while cleavage to the mononuclear species is insignificant (eq 10). The

$$(en)_2Rh(OH)_2Rh(en)_2^{4+} + H_3O^+ \rightarrow (H_2O)(en)_2Rh(OH)Rh(en)_2(H_2O)^{5+} \quad (10)$$

mixture was then quenched by cooling and neutralized, and the perchlorate salt, $\Delta,\Delta/\Lambda,\Lambda$-$[(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)](ClO_4)_4{\cdot}H_2O$, was precipitated. A pure sample was obtained after three further reprecipitations (yield 25% based upon *cis*-$[Rh(en)_2(H_2O)(OH)](S_2O_6)$). The purity was examined by HPLC, which was carried out at 0 °C in order to prevent formation of the dihydroxo-bridged species during chromatography. The HPLC analysis showed that the compound was more than 99.5% pure; it was estimated that a small peak corresponding to 0.5% of $\Delta,\Delta/\Lambda,\Lambda$-$(en)_2Rh(OH)_2Rh(en)_2^{4+}$ probably was due to the formation of this species during the analytical procedures rather than due to its presence in the solid sample (Figure 5).

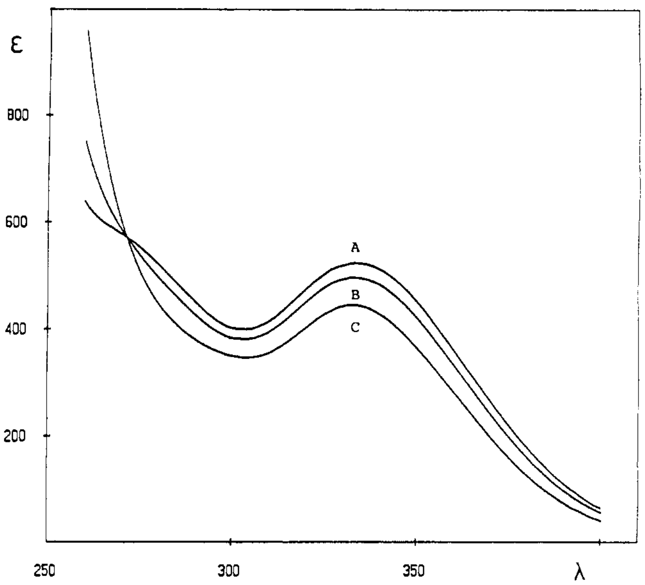

Figure 4. Absorption spectra of the pure species $\Delta,\Delta/\Lambda,\Lambda$-$(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)^{4+}$ (A) and $\Delta,\Delta/\Lambda,\Lambda$-$(en)_2Rh(OH)Rh(en)_2^{4+}$ (C) obtained by extrapolation back to the time of dissolution, and the spectrum of the solution containing these species in equilibrium (B) in 1 M $NaClO_4$ at 25 °C.

The solid salt $\Delta,\Delta/\Lambda,\Lambda$-$[(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)](ClO_4)_4{\cdot}H_2O$ is stable at room temperature for months, but at high temperature it is converted to the corresponding dihydroxo-bridged complex. Heating for 70 h at 140 °C gave pure (99%) $\Delta,\Delta/\Lambda,\Lambda$-$[(en)_2Rh(OH)_2Rh(en)_2](ClO_4)_4$. The presence of the Δ,Λ-isomer could not be detected and thus was less than 1%.[12]

Absorption Spectra of the Racemic Isomers. The absorption spectra of $\Delta,\Delta/\Lambda,\Lambda$-$(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)](ClO_4)_4{\cdot}H_2O$ were measured in the $[H^+]$ region $10^{-13} \le [H^+] \le 1.0$ M. All spectral measurements, extrapolated to t_0, could be interpreted in terms of the two consecutive acid–base equilibria given in eq 11 and 12. These observations strongly support the

$$\Delta,\Delta/\Lambda,\Lambda\text{-}(H_2O)(en)_2Rh(OH)Rh(en)_2(H_2O)^{5+} \rightleftarrows \Delta,\Delta/\Lambda,\Lambda\text{-}(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)^{4+} + H^+ \quad (11)$$

$$\Delta,\Delta/\Lambda,\Lambda\text{-}(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)^{4+} \rightleftarrows \Delta,\Delta/\Lambda,\Lambda\text{-}(OH)(en)_2Rh(OH)Rh(en)_2(OH)^{3+} + H^+ \quad (12)$$

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(11) These ΔH° and ΔS° values have been calculated from our previously published[8] pK_a values determined at 25 °C and additional values for 40 °C determined in this study.

(12) When solutions of the dihydroxo-bridged species are analyzed by HPLC, it is difficult to detect a small amount of the Δ,Λ isomer in the $\Delta,\Delta/\Lambda,\Lambda$ isomer and vice versa. However, if such solutions are kept for $1^1/_2$ h at room temperature, a significant amount of the respective monohydroxo-bridged species is formed (~92% Δ,Λ and ~65% $\Delta,\Delta/\Lambda,\Lambda$), and the HPLC peaks for these species are well separated. For this technique, it was estimated that a contamination of one isomer with 1% of the other would be detected.

Table IV. Thermodynamic and Kinetic Data for the Equilibrium[a]

$$(en)_2M(OH)_2M(en)_2^{4+} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (H_2O)(en)_2M(OH)M(en)_2(OH)^{4+}$$

M	confign	K_1	$\Delta H°$/ kJ mol^{-1}	$\Delta S°$/ J mol^{-1} K^{-1}	k_1/s^{-1}	$\Delta H^{\ddagger}(k_1)$/ kJ mol^{-1}	$\Delta S^{\ddagger}(k_1)$/ J mol^{-1} K^{-1}	k_{-1}/s^{-1}	$\Delta H^{\ddagger}(k_{-1})$/ kJ mol^{-1}	$\Delta S^{\ddagger}(k_{-1})$/ J mol^{-1} K^{-1}
Rh(III)	Δ,Λ	11.2 (3)[b]	−14 (3)	−27 (4)	$4.6 (1) \times 10^{-4}$	86 (3)	−19 (8)	$4.1 (1) \times 10^{-5}$	101 (3)	9 (9)
Rh(III)	Δ,Δ/Λ,Λ	1.89 (4)[c]	−9 (1)	−23 (4)	$5.3 (1) \times 10^{-4}$	75 (3)	−57 (9)	$2.81 (5) \times 10^{-4}$	83 (3)	−33 (9)
Cr(III)	Δ,Λ	0.75 (2)[d]	−3 (1)	−13 (3)	$6.9 (5) \times 10^{-3}$	80 (2)	−18 (7)	$9.3 (7) \times 10^{-3}$	84 (2)	−1 (7)
Cr(III)	Δ,Δ/Λ,Λ	0.22 (3)[e]	−2 (4)	−19 (13)	$4.6 (2) \times 10^{-3}$	85 (1)	−4 (5)	$2.1 (1) \times 10^{-2}$	87 (1)	15 (5)

[a] 25 °C, 1 M $NaClO_4$. [b] From ref 8. See also footnote to Table I. [c] This work. [d] From ref 13 and 15. [e] From ref 14 and 15.

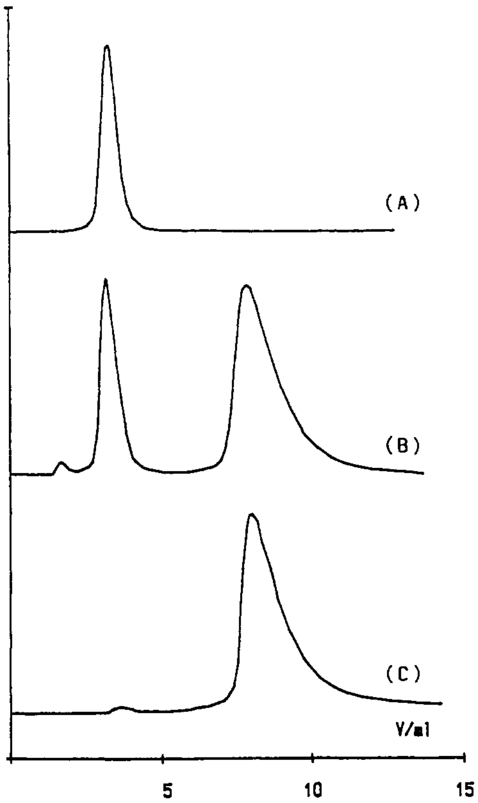

Figure 5. HPLC chromatograms (measured at 0 °C) for solutions of Δ,Δ/Λ,Λ-$[(en)_2Rh(OH)_2Rh(en)_2](ClO_4)_4$ (A) and Δ,Δ/Λ,Λ-$[(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)](ClO_4)_4 \cdot H_2O$ (C), and for an equilibrium solution in 1 M $NaClO_4$ made at 25 °C (B).

proposed monohydroxo-bridged structure. Spectral data for the three species are given in Table III.

The spectra of Δ,Δ/Λ,Λ-$[(en)_2Rh(OH)_2Rh(en)_2](ClO_4)_4$ in 1 M $NaClO_4$ and 1 M $HClO_4$, both extrapolated to t_0, are identical, which supports the proposed dihydroxo-bridged structure (Table III).

Equilibrium between the Racemic Isomers. It was recently shown[8] that the Δ,Λ-isomers of the dinuclear species equilibrate as shown in Scheme I. In the present study the corresponding Δ,Δ/Λ,Λ-isomers were found to react similarly. The equilibrium constant K_1(Δ,Δ/Λ,Λ) was determined at 25.0, 40.0, and 60.0 °C on the basis of spectrophotometric measurements, as described above. This gave the values shown in Table IV (see also Figure 4). Analysis of the equilibrium solutions by HPLC confirmed this result. Identical elution curves were obtained for equilibrium solutions initially containing either the monohydroxo- or dihydroxo-bridged species (Figure 5). From the ratio between the peak areas for the two species the equilibrium constant was calculated. This gave K_1(Δ,Δ/Λ,Λ) = 2.1 (1) at 25 °C, to be compared with the value 1.89 (4) determined spectrophotometrically (Table IV). Likewise, K_1(Δ,Λ) = 9.3 (10) at 25 °C was determined by HPLC experiments, this value being close to the value of 11.2 (3) previously determined by spectrophotometry.[8]

The kinetics of the equilibration reaction between the racemic isomers were studied spectrophotometrically at 25 and 40 °C. From the observed rate constants, k_{obs}, the rate constants k_1(Δ,Δ/Λ,Λ) and k_{-1}(Δ,Δ/Λ,Λ) were calculated as described above (see Table IV).

In acidic solutions, the cleavage reaction yields the monohydroxo-bridged species nearly quantitatively, as shown spectrophotometrically (see eq 10). At 1.0 °C the following rate constants have been determined spectrophotometrically, starting with the dihydroxo-bridged species: $k_{obs} = 7.8 \times 10^{-3}$ s^{-1} in 1 M $HClO_4$ and $k_{obs} = 7.2 \times 10^{-4}$ s^{-1} in 0.1 M $HClO_4$, 0.9 M $NaClO_4$. The rate constant for the uncatalyzed bridge-cleavage reaction is calculated from the parameters in Table IV to be $k_1 = 3.5 \times 10^{-5}$ s^{-1} at 1.0 °C. The increased rate in acidic solutions clearly demonstrated the presence of an acid-catalyzed pathway, as has also been reported for the corresponding meso isomers.[8]

Assignment of Structures. On the basis of the properties mentioned above, assignment of the structure of the new racemic species can be made as follows. From the elemental analyses and the acid–base properties (spectral changes with pH), it is shown that the new complexes, I from preparation 1 and II from preparation 2, contain one hydroxo bridge and two hydroxo bridges per two rhodiums, respectively. The equilibrium studies unambiguously establishes that the nuclearity of the two new complexes is the same as that of the known meso isomers [the ratio between the equilibrium concentrations of the polynuclear species is unchanged, when the rhodium(III) concentration is varied by more than a factor of 100]. It therefore follows that the new species both are dinuclear. The presence of two hydroxo bridges in II thus requires that the configuration around both rhodium(III) centers must be cis; i.e., the structure is either Δ,Λ- or Δ,Δ/Λ,Λ-$(en)_2Rh(OH)_2Rh(en)_2^{4+}$. Since II is different from the known meso isomer, it must be the racemic form. Finally, the interpretation of the relatively fast equilibration reaction between I and II in terms of hydroxo bridge cleavage and formation, and thereby also the structure assignment of I, is in keeping with the large body of knowledge of this type of reaction involving metal centers such as cobalt(III), rhodium(III), iridium(III), and chromium(III).[4] The assumption that this reaction occurs with retention of configuration is based upon the well-known reluctance of rhodium(III) ammine and amine complexes to undergo isomerization by thermal substitution reactions.[4]

It is noted that the present dinuclear complexes all have cis configuration around both metal centers. Since the cis configuration is implied by the chirality symbols Δ and Λ, we have followed the common use of omitting cis,cis in the formulas.

The idea that the new dinuclear compounds could be geometric isomers of the type cis,trans or trans,trans can be ruled out for the reasons given above. Also the following evidence points heavily toward the assumption that no isomerization takes place. The equilibrium solutions of mononuclear and dinuclear species contain *cis*-$Rh(en)_2(H_2O)(OH)^{2+}$, but no trans isomer, as shown by HPLC. This is strong evidence against the presence of dinuclear species having trans configuration at one or both of the rhodium(III) centers. Finally, there is good evidence[4] that dinuclear species of the type $(H_2O)L_4M(OH)ML_4(OH)^{z+}$ with configuration cis,trans or trans,trans have much smaller formation constants than cis,cis species, which is in agreement with the present results.

We therefore consider the structure assignments of the two new racemic dinuclear species to be unambiguous.

Discussion

The hydrolysis of *cis*-$Rh(en)_2(OH)(H_2O)^{2+}$ in aqueous solution was previously shown to give only dinuclear species containing one or two hydroxo bridges, viz. the meso (Δ,Λ) and the racemic (Δ,Δ/Λ,Λ) isomers of $(H_2O)(en)_2Rh(OH)Rh(en)_2(OH)^{4+}$ and $(en)_2Rh(OH)_2Rh(en)_2{}^{4+}$. In the present study this has been further and unambiguously established both by the successful isolation of the new racemic isomers as pure and stable solid salts and by quantitative analysis of the equilibrium solutions by HPLC.

In our previous study we determined the gross equilibrium constant K_D (eq 7), and by assuming that the meso and racemic isomers were equally stable, we could obtain an estimate for the dimerization constants $K_d(\Delta,\Lambda)$ and $K_d(\Delta,\Delta/\Lambda,\Lambda)$. Combination of the present quantitative analyses of the equilibrium solutions by HPLC with our previously determined values for K_D has made it possible to determine accurately the constants given in Table II.

The value of $K_d(\Delta,\Lambda)$ is close to the value estimated previously, and our previous discussion of the kinetics and thermodynamics of the dimerization of *cis*-$Rh(en)_2(H_2O)(OH)^{2+}$ to give meso dinuclear species is therefore still valid. From Table II, it is seen that $\Delta H°(K_d)$ and $\Delta S°(K_d)$ are very similar for the meso and racemic isomers, and this follows the lines given below for K_{isom}.

The values $K_{isom}(M) = 0.32$ (2) and $K_{isom}(D) = 1.9$ (5) at 25 °C are both significantly different from the statistically expected value of 0.5. It is seen that the difference in the stability of the Δ,Δ isomers relative to the Δ,Λ isomers is reversed on going from the monohydroxo-bridged species to the dihydroxo-bridged species. However, the difference in stability of the diastereoisomers is small. For both equilibria, $\Delta H°$ is close to zero, as would be expected for reactions in which similar bonds are broken and formed. The values of $\Delta S°$ are comparable to the statistically expected value of $-R \ln 2 = -6$ J mol^{-1} K^{-1}. The corresponding chromium(III) species have also been characterized, and for the species $(HO)(en)_2Cr(OH)Cr(en)_2(OH)^{3+}$, the ratio Δ,Δ/Δ,Λ was found to be 2 (1) at 45 °C in 7 M aqueous 1,2-ethanediamine.[13]

For both Rh(III) and Cr(III), it may therefore be concluded that the diastereoisomers are roughly equally stable for singly bridged as well as for doubly bridged binuclear species. This strongly indicates that intramolecular interactions (such as hydrogen-bond formation or repulsion between the hydrogen atoms at the "axial" nitrogen ligators) are similar in the diastereoisomers, as also indicated by molecular models.

The observation that the experimentally determined constant K_{RM} does not change when the ionic strength is varied from 1.0 to 5 M strongly indicates that the equilibrium constants K_1 and K_{isom} (which define K_{RM}) have a small ionic strength dependence. K_1 refers to a reaction between an uncharged molecule and a cation (k_1) and to an intramolecular reaction (k_{-1}). The ionic strength dependence of K_1 should therefore be small, as also previously confirmed experimentally for the reactions of the corresponding meso chromium(III) species.[14] K_{isom} refers *formally* to intramolecular rearrangements and is therefore also expected to be very insensitive to the ionic strength.

The equilibrium between the mono- and dihydroxo-bridged species was previously studied for the meso isomers, and it was shown that the equilibrium reaction may proceed by an uncatalyzed and an acid-catalyzed pathway.[8] The present racemic system behaves similarly, but only the uncatalyzed pathway has been studied in detail. Table IV summarizes the thermodynamic and kinetic data obtained in this work for the racemic system and those previously determined for the meso system. Also included in the table are the data reported for the corresponding chromium(III) species.[13-15]

The thermodynamic parameters $\Delta H°(K_1)$ and $\Delta S°(K_1)$ are roughly equal for the meso and the racemic isomers of either rhodium(III) or chromium(III). This result follows the discussion of K_{isom} given above. It is, however, noted that $K_1(\Delta,\Lambda)$ is greater than $K_1(\Delta,\Delta/\Lambda,\Lambda)$ for both metal ions by almost the same factor (6 and 4, respectively). The steric interactions, which probably cause these small but significant variations, therefore seem to be the same in the two systems.

While the thermodynamic parameters show similar trends for the two metal ions, this does not seem to be the case with the kinetic data. Inspection of Table IV shows that the activation parameters for the reactions of the meso and the racemic isomers of the rhodium(III) species are different. For both k_1 and k_{-1} it is found that $\Delta H^*(\Delta,\Lambda) > \Delta H^*(\Delta,\Delta/\Lambda,\Lambda)$ and $\Delta S^*(\Delta,\Lambda) > \Delta S^*(\Delta,\Delta/\Lambda,\Lambda)$. For the corresponding reactions of the chromium(III) analogues, the difference is much less and the order is reversed: $\Delta H^*(\Delta,\Lambda) \leq \Delta H^*(\Delta,\Delta/\Lambda,\Lambda)$ and $\Delta S^*(\Delta,\Lambda) \leq \Delta S^*(\Delta,\Delta/\Lambda,\Lambda)$. The kinetic similarity of the reactions of the isomers of chromium(III) follows the thermodynamic result presented above. The significantly different kinetic behavior of the isomers of rhodium(III) is surprising, and at present we do not understand these differences.

Summary. The thermodynamic data for isomerization between the dinuclear rhodium(III) species (containing one or two hydroxo bridges) studied in the present work show that meso and racemic isomers are almost equally stable. This result is in keeping with previous studies of the chromium(III) analogues and indicates that intramolecular interactions are similar in the corresponding diastereoisomers of both metal ions. The kinetic data for intramolecular bridge formation and bridge cleavage show a difference between the isomers, and this difference is more pronounced for rhodium(III) than for chromium(III).

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