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

Johan Springborg

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

Springborg, J., 1992. Formation and Cleavage of Hydroxo-Bridged Binuclear Rhodium(III) Ammine Complexes. – Acta Chem. Scand. 46: 956–963.

The equilibration between the mononuclear species *cis*-$Rh(NH_3)_4(H_2O)_2{}^{3+}$ (and its deprotonated forms) and the binuclear species *cis,cis*-$(H_2O)(NH_3Rh(OH)Rh(NH_3)_4(OH)^{4+}$ (and deprotonated forms) and $(NH_3)_4Rh(OH)_2Rh(NH_3)_4{}^{4+}$ has been studied at 25.0, 40.0, 60.00, 80.0 and 100.0 °C in 1 M (Na,H)ClO_4 with $[H^+] = 10^{-7}$–1.0 M using spectrophotometry, supplemented with IE–HPLC studies. The results are interpreted in terms of the equilibria given in the paper. Data for the equilibration between the binuclear species have been published previously, and in the present study the thermodynamic (K_3/K_{a3}, K_4 and K_5) and kinetic (k_3/K_{a3}, k_4, k_5 and k_{-3}, k_{-4} and k_{-5}) data are given for the equilibration between mononuclear and binuclear species. Kinetic data for the dimerization processes (k_{-3}, k_{-4} and k_{-5}) for the corresponding Δ,Λ binuclear species with 1,2-ethanediamine have been calculated on the basis of data published previously.

Hydrolysis of aquated 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 reactions are of relevance to solid-state physics and geological processes (properties and formation of oxides) and biology (many metalloproteins contain hydroxo-bridged binuclear metal cenres). The kinetics for cleavage of hydroxo bridges have been studied in detail for several transition metals, as also have the kinetics of the intramolecular hydroxo bridge formation. Intermolecular hydroxo bridge formation reactions have been far less studied. The first and fundamental reaction initiating these polymerizations is the condensation of two monomeric species, and kinetic studies for this reaction are few and rather unsystematic.[2]

We have recently studied the cleavage of the meso isomers of the binuclear species Δ,Λ-$(H_2O)(en)_2Rh(OH)Rh(en)_2(H_2O)^{5+}$ (and its deprotonated forms) to mononuclear species in acidic solutions.[3] The equilibrium constants for the equilibria between mono- and binuclear species were also determined, and it was therefore possible to estimate the rate constants for the dimerization reactions. The latter estimate was, however, encumbered with some error, since the ratio between meso and racemic isomers of the binuclear species was unknown, and it was assumed that they were nearly equally stable. This has later been confirmed in a recent study.[4] It was shown that the content of mononuclear species and both meso (Δ,Λ) and racemic (Δ,Δ/Λ,Λ) binuclear species in the equilibrium solutions could be determined quantitatively using IE-HPLC, and on this basis a reasonably accurate estimate of the formation constants for both isomers was obtained. Combination of these new thermodynamic data with the kinetic data for the cleavage reaction now permits the kinetic data for the dimerization reactions (to give meso isomers) to be calculated, as shown in the present study. In continuation of our studies of the amine system we iniated a study of the corresponding ammine system, which is much simpler because of the absence of optical isomers. The equilibrium between the monohydroxo- and dihydroxo-bridged species has been studied previously,[5] and in the present study we report our results for the thermodynamics and kinetics of the equilibria between the mono- and binuclear ammine rhodium(III) species.

Experimental

Materials and instruments. The complexes *cis*-$[Rh(NH_3)_4(H_2O)(OH)]S_2O_6$, *trans*-$[Rh(NH_3)_4(H_2O)(OH)](ClO_4)_2$, *cis,cis*-$[(HO)(NH_3)_4Rh(OH)Rh(NH_3)_4(H_2O)](ClO_4)_4 \cdot H_2O$ and $[(NH_3)_4Rh(OH)_2Rh(NH_3)_4](ClO_4)_4$ were synthesized as described previously.[6,7] All reagents were of analytical grade, and CO_2-free doubly deionized water was used for all measurements. A Perkin-Elmer diode-array spectrophotometer was used for spectral measurements. The molar absorption coefficient ε is given in dm^3 [mol Rh(III)]$^{-1}$ cm^{-1} for both mononuclear and binuclear species, and the wavelength λ is given in nm. The pH measurements (Radiometer equipment) and the ion-exchange high-performance liquid chromatography (IE–HPLC, Waters equipment) were performed as described previously.[4,5]

Synthesis of cis-*$[Rh(NH_3)_4(H_2O)(OH)](ClO_4)_2$.* A mixture of *cis*-$[Rh(NH_3)_4(H_2O(OH)]S_2O_6$ (2 g, 5.5 mmol) and an aqueous saturated solution of $NaClO_4$ (50 ml) was stirred at

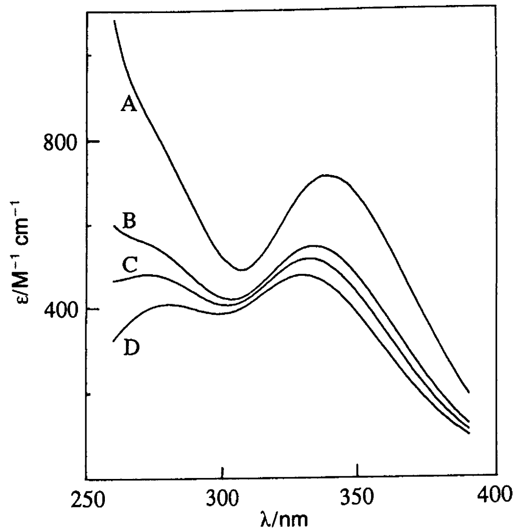


Fig. 1. Absorption spectra of an equilibrium mixture of the binuclear species (**A**), the mononuclear species (**D**), and of equilibrium mixtures of the mononuclear and binuclear species made at 100 °C using C_{Rh} = 0.018 M (**B**) and C_{Rh} = 0.005 M (**C**), in 1 M $NaClO_4$.

room temperature for 1 h. The precipitate was filtered off, dissolved in water (200 ml), and then an aqueous saturated solution of $NaClO_4$ (200 ml) was added to the filtered solution. After a few minutes the precipitate was filtered off, washed twice with 5 ml 50 % ethanol, three times with 10 ml 96 % ethanol, and then dried in the air. Yield 1.1 g (50 %) of pure *cis*-$[Rh(NH_3)_4(H_2O)(OH)](ClO_4)_2$. The VIS–UV spectrum was identical with that previously reported for the dithionate salt.[6] The IE–HPLC elution curve was identical with that of pure *cis*-$[Rh(NH_3)_4(H_2O)(OH)]S_2O_6$ and showed that the product was more than 99.5 % pure.

Determination of acid dissociation constants. The second concentration acid dissociation constant, $K_{a2}{}^{d}$, of *cis,cis*-$(H_2O)(NH_3)_4Rh(OH)Rh(NH_3)_4(H_2O)^{5+}$ was determined by glass-electrode measurements as described previously for its determination at 25 °C.[5] This gave $pK_{a2}{}^{d}$ = 8.505(2) at 40.0 °C, which, together with the value determined previously at 25 °C, gave the thermodynamic parameters given in Table 1.

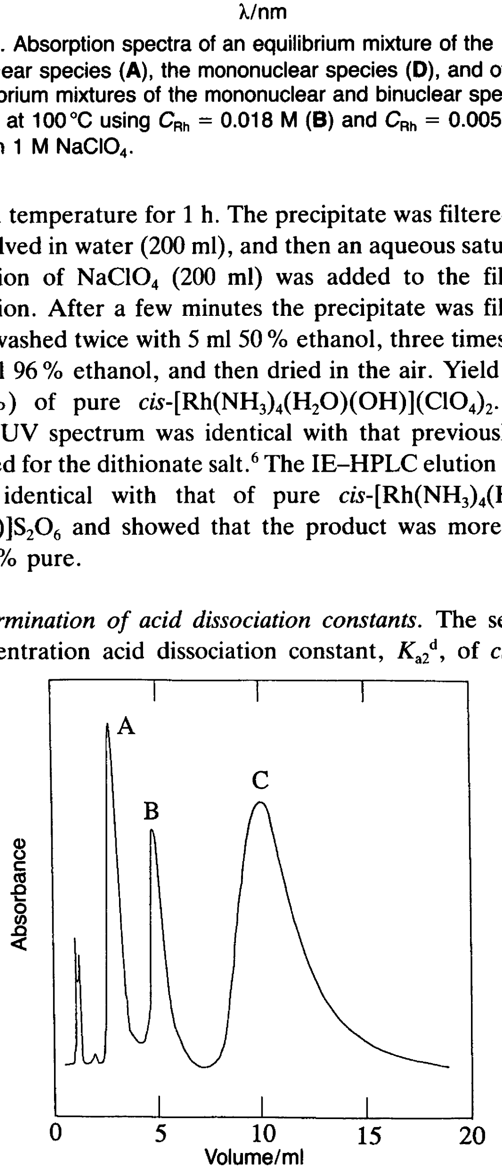


Fig. 2. IE–HPLC: elution curve of an equilibrium mixture of the mononuclear and binuclear species made at 60 °C with C_{Rh} = 0.25 M. (**A**) *cis*-$Rh(NH_3)_4(H_2O)(OH)^{2+}$, (**B**) $(NH_3)_4Rh(OH)_2Rh(NH_3)_4{}^{4+}$ and (**C**) *cis,cis*-$(H_2O)(NH_3)_4Rh(OH)Rh(NH_3)_4(OH)^{4+}$.

Determination of K_5 *by spectrophotometry.* Equilibrium solutions were obtained by heating solutions of either *cis*-$[Rh(NH_3)_4(H_2O)(OH)](ClO_4)_2$ or $[(NH_3)_4Rh(OH)_2Rh(NH_3)_4](ClO_4)_4$ in 1 M $NaClO_4$, kept in glass ampoules, at 60.0, 80.0 and 100 °C for 210, 18 and 3 h, respectively. It was not possible to measure the absorption spectra at the equilibrium temperatures owing to an ineffective thermostatting of the cell compartment at the highest temperatures. Instead, all spectra were measured at 40 °C after the solutions had been kept for 7 h at this temperature. During this time re-equilibration between the monohydroxo- and dihydroxo-bridged species (K_1) is established ($t_{1/2}$ = 1 h),[5] while the reactions between the mono- and binuclear species are insignificant, as can be seen from the kinetic data in the present work. The concentration of the sum of the mononuclear species, C_m, and the sum of the binuclear species, C_d, was calculated from the absorption spectra using eqn. (1).

$$C_d/C_m = (\varepsilon_{eq} - \varepsilon_{monomer})/2(\varepsilon_{dimer} - \varepsilon_{eq}) \qquad (1)$$

In eqn. (1) $\varepsilon_{monomer}$, ε_{dimer} and ε_{eq} are the molar absorbances of a solution of *cis*-$[Rh(en)_2(H_2O)(OH)](ClO_4)_2$, an equilibrium solution of the monohydroxo- and dihydroxo-bridged binuclear species, and the re-equilibrated equilibrium solutions, respectively, all measured at 40 °C. These calculations were in each experiment based upon absorbances measured at 131 different wavelengths in the region 260–390 nm. Additional experiments in which the solutions were heated for longer periods gave the same result. The actual concentrations of *cis*-$Rh(NH_3)_4(H_2O)(OH)^{2+}$ and *cis,cis*-$(H_2O)(NH_3)_4Rh(OH)Rh(NH_3)_4(OH)^{4+}$ in the original equilibrium solutions (60.0, 80.0 and 100 °C) were then calculated using the known equilibrium constants for the relevant acid–base equilibria (Table 1) and the equilibrium constant for the equilibrium between the monohydroxo- and dihydroxo-bridged species: K_1 = 3.029(38), $\Delta H°$ = 1.63(115) kJ mol^{-1} and $\Delta S°$ = 14.67(377) J mol^{-1} K^{-1} (from Ref. 5, but to more decimal places than given in this reference, calculated from the original data). This gave the results shown in Tables 2 and 3; see also Fig. 1.

Determination of K_5 *by IE–HPLC measurements.* Equilibrium solutions made as described above were analyzed following the same procedure as described previously[4] for the analogous 1,2-ethanediamine system. The concentrations of the mononuclear species and of the monohydroxo- and dihydroxo-bridged species were calculated from the relative peak areas, and the equilibrium constant K_5 was then calculated as above (Fig. 2).

Table 1. Acid dissociation constants for the mononuclear and binuclear species in 1 M $NaClO_4$ and at 25 °C.[a]

Complex	pK_a[b]	$\Delta H°$ /kJ mol^{-1}	$\Delta S°$ /J mol^{-1} K^{-1}	Ref.
cis-$Rh(NH_3)_4(H_2O)_2^{3+}$	6.391(9)	44.9(16)	28(5)	10
	8.356(7)	42.6(11)	−17(4)	10
cis,cis-$(H_2O)(NH_3)_4Rh(OH)Rh(NH_3)_4(H_2O)^{5+}$	3.406(8)	52.6(16)	111(5)	5
	8.797(14)	34.8(17)	−52(5)	5[c]
cis-$Rh(en)_2(H_2O)_2^{3+}$	6.338(2)	43.2(6)	23(2)	11
	8.244(2)	41.9(8)	−17(3)	4, 11
Δ,Λ-$(H_2O)(en)_2Rh(OH)Rh(en)_2(H_2O)^{5+}$	2.372(7)	28(4)	49(13)	11
	9.128(7)	39.5(6)	−42(2)	4, 11

[a] Standard deviations have been given in parentheses in units of the last digit. [b] $pK_a = -\log(K_a/M)$. [c] From data determined at 25 °C in Ref. 5 supplemented with new data at 40 °C made in the present study.

Kinetic measurements. Reactant solutions were made by dissolving $[(NH_3)_4Rh(OH)_2Rh(NH_3)_4](ClO_4)_4$ in 1 M $(Na,H)ClO_4$ solution. For the conditions used, the reaction to mononuclear species has half-lives from minutes to 10 days. Some kinetic experiments were based upon repetitive scanning of the absorption spectra, but most experiments were made using aliquots of the solution, kept separately in glass ampoules in the dark. Pseudo-first-order rate constants, k_{obs}, were calculated as described previously.[5] In each kinetic run the rate constants were calculated on the basis of absorbances measured at 131 different wavelengths in the region 260–390 nm.

The hydrogen-ion concentration changed slightly during a kinetic experiment. The hydrogen-ion concentration in the original equilibrated solutions of binuclear species, $[H^+]_0$, and in the final solutions of mononuclear species, $[H^+]_{eq}$, was calculated from the solution stoichiometry using the thermodynamic parameters given in Table 1 and the values of K_1 given above. For solutions with $[H^+]_0 > 10^{-2}$ M, the variations of the hydrogen-ion concentration were < 2%. At lower $[H^+]$, larger variations were calculated (5% for $[H^+]_0 = 0.005$ M and $C_{Rh} = 1.8 \times 10^{-3}$ M), but in this region the observed dependence of k_{obs} on $[H^+]$ is small. For solutions in pure 1 M $NaClO_4$, it was found by glass-electrode measurements that pH in the product solutions was 7.5, which is close to the theoretical value (7.4 at 25.0 °C) calculated from the data in Table 1. It is therefore concluded that the variations in $[H^+]$ during a single experiment can be ignored and that pseudo first-order conditions can be assumed. The value $[H^+] = 1/2([H^+]_0 + [H^+]_{eq})$ was then used in the following calculations.

Table 2. Spectrophotometric determination of K_5 in 1 M $NaClO_4$.

T/°C	C_{Rh}/M	K_5(obs)/M	K_5(calc)[a]/M
100.0	0.018	0.0382	0.0369
100.0	0.010	0.0385	–
100.0	0.010[b]	0.0329	–
100.0	0.005	0.0357	–
80.0	0.01	0.0327	0.0298
80.0	0.01	0.0311	–
60.0	0.01	0.0223	0.0235
60.0	0.01	0.0232	–

[a] The values of K_5 have been obtained by non-linear regression analysis which gave the thermodynamic parameters in Table 3. [b] In this experiment the equilibrium solution was made by starting with a solution of monomer, while all the other solutions were made starting with the salt of the binuclear species.

The activation parameters were fitted by minimizing the sum of $(\ln k_{obs} - \ln k_{calc})^2$, the values of k_{calc} being defined by eqn. (2) and $k = (k_B T/h) \exp(\Delta S^{\ddagger}/R - \Delta H^{\ddagger}/RT)$ (Table 4 and Fig. 3).

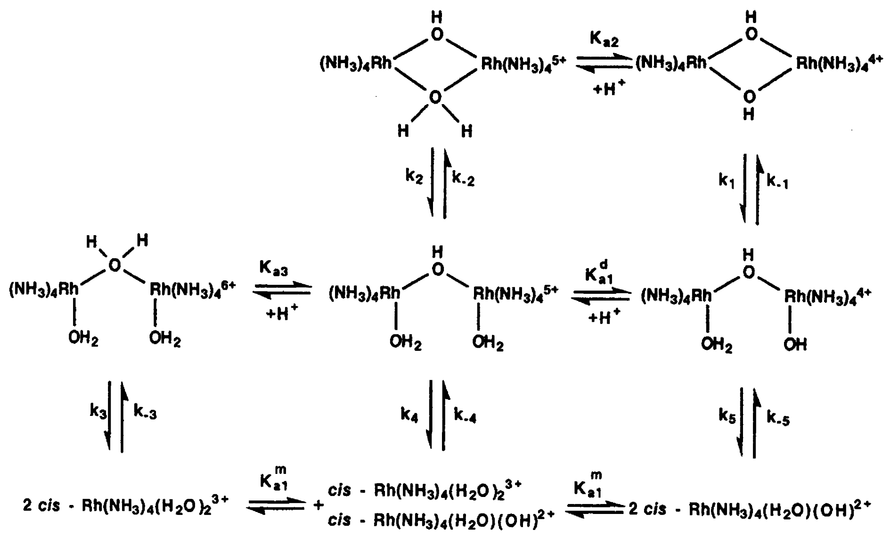
Results

Equilibrium studies. The $(NH_3)_4Rh(OH)_2Rh(NH_3)_4^{4+}$ ion undergoes bridge cleavage in neutral and acidic solution to

Table 3. Thermodynamic data for the equilibria between mononuclear and binuclear species at 25 °C in 1 M $NaClO_4$.

Reaction		*K* /M or 1	$\Delta H°$ /kJ mol^{-1}	$\Delta S°$ /J mol^{-1} K^{-1}
K_3/K_{a3}	(NH_3)	$3.6(8) \times 10^7$	−25.5(31)	59.2(86)
	(en)	$1.4(3) \times 10^8$	−42(5)	18(16)
	–	$[2.8(6) \times 10^8]$		[24(16)]
K_4	(NH_3)	14.3(30)	19.4(27)	87.2(70)
	(en)	65(13)	2(5)	41(16)
	–	[130(26)]		[47(16)]
K_5	(NH_3)	$14.3(15) \times 10^{-3}$	11.7(16)	3.9(44)
	(en)	$7.0(20) \times 10^{-3}$	17(3)	14(9)
	–	$[14(4) \times 10^{-3}]$		[20(4)]
K_6	(NH_3)	$4.0(5) \times 10^{-2}$	19.5(26)	38.9(78)
	(en)	$5.4(7) \times 10^{-2}$	19(3)	40(10)
	–	$[10.8(14) \times 10^{-2}]$		[46(10)]

[a] The parameters for the ammine system are defined as shown in Scheme 1 and eqn. (2). The parameters for the 1,2-ethanediamine complexes are defined as shown in the Appendix, and have been calculated from data in Ref. 4. Statistically corrected values, given in square brackets, have been calculated as shown in the Appendix.



Scheme 1. Reaction scheme for the equilibrium between mononuclear and binuclear species.

give the mononuclear species *cis*-$Rh(NH_3)_4(H_2O)_2^{3+}$ and its deprotonated forms. The bridge cleavage occurs in two kinetically well separated steps. Equilibrium between the monohydroxo- and dihydroxo-bridged species in acidic and neutral solution has previously been shown to involve the equilibria shown in the upper part of Scheme 1.[5] In the present work the equilibria between the mononuclear and binuclear species have been studied (lower part of Scheme 1). In acidic solution these equilibria are shifted almost completely to the mononuclear species (see also below), and spectroscopic determination of the equilibrium constants is therefore not possible in this region. Equilibrium studies were therefore restricted to almost neutral solutions, which for large rhodium(III) concentrations contain significant amounts of both mononuclear and binuclear species. The equilibrium solutions were analyzed by spectral measurements in the VIS–UV region and by ion-exchange high-performance liquid chromatography (IE-HPLC).

Equilibrium solutions were obtained by heating solutions of either *cis*-$[Rh(NH_3)_4(H_2O)(OH)](ClO_4)_2$ or $[(NH_3)_4Rh(OH)_2Rh(NH_3)_4](ClO_4)_4$ in 1 M $NaClO_4$, as described in the Experimental section. The spectra were identical for solutions initially containing mononuclear and binuclear species, respectively, and they could be reproduced as linear combinations of the spectrum of *cis*-$[Rh(NH_3)_4(H_2O)(OH)](ClO_4)_2$ in 1 M $NaClO_4$ and the spectrum of an equilibrium mixture of the binuclear species in 1 M $NaClO_4$ (curves A and D in Fig. 1). It is therefore concluded that the stoichiometry can be expressed as the bridge-cleavage reactions together with the relevant acid–base reactions shown in Scheme 1. The equilibrium constant K_5 was then calculated from the spectra as described in the Experimental section. It is seen that there is reasonable agreement between the observed and calculated constants (Table 2) and that the parameters $\Delta H°$ and $\Delta S°$ are well defined (Table 3). The other equilibrium constants, K_3, K_4 and K_6, were calculated as described in the Appendix. [K_3 and K_4 are defined in Scheme 1 and K_6 is defined in eqn. (2).]

$$K_6 = \frac{[cis\text{-}Rh(NH_3)_4(H_2O)(OH)^{2+}][cis\text{-}Rh(NH_3)_4(OH)_2^{+}]}{[cis,cis\text{-}(OH)(NH_3)_4Rh(OH)Rh(NH_3)_4(OH)^{3+}]} \quad (2)$$

The above result was confirmed by IE-HPLC analysis of an equilibrium solution with $C_{Rh} = 0.25$ M made at 60 °C. As seen from Fig. 2, the equilibrium contains three major components, identified as *cis*-$Rh(NH_3)_4(H_2O)(OH)^{2+}$, *cis,cis*-$(H_2O)(NH_3)_4Rh(OH)Rh(NH_3)_4(OH)^{4+}$ and $(NH_3)_4Rh(OH)Rh(NH_3)_4^{4+}$, respectively, by comparison with the elution curves of the authentic species. Furthermore, it was shown that this analysis can clearly distinguish the *cis* and *trans* isomers of the mononuclear species. The IE-HPLC analysis therefore shows that the content of the *trans* isomers in the equilibrium mixture must be negligible. The minor peaks in the front of the elution curve are probably carbonato complexes, as discussed previously in connection with the analogous 1,2-ethaneiamine system, but were not further identified. The equilibrium constant K_5 was then calculated from the relative peak areas. This gave $K_5 = 0.019$ M, which is in reasonable agreement with the spectroscopically determined value $K_5 = 0.023$ M (60 °C). The difference between the two values is probably mainly due to the difference in ionic strength, which is 1.0 M for the spectroscopically determined value, while it is significantly larger than one for the IE-HPLC experiment because of the large concentration of complex ($C_{Rh} = 0.25$ M). It should be noted that the same experiment gave $K_1 = 3.0$, which is in agreement with the more accurate value $K_1 = 3.25(0.12)$ reported[5] previously. (Since K_1 refers to a reaction between equally charged complexes, it is expected to show only a small dependence on the ionic strength.)

Kinetics of the cleavage of singly bridged species. The cleavage of the monohydroxo-bridged species to give the mono-

Table 4. Kinetic data for the equilibration between mononuclear and binuclear species at 25 °C in 1 M $NaClO_4$.[a]

Reaction		k /s^{-1} or M^{-1} s^{-1}	$\Delta H^‡$ /kJ mol^{-1}	$\Delta S^‡$ /J mol^{-1} K^{-1}
k_3/K_{a3}	(NH_3)	$2.21(10)\times10^{-5}$	76.9(15)	−76.2(48)
	(en)	$3.48(15)\times10^{-5}$	78(4)	−68(14)
k_4	(NH_3)	$3.78(40)\times10^{-7}$	121.7(23)	40.2(68)
	(en)	$1.91(8)\times10^{-6}$	116(3)	34(10)
	–	$[3.82(15)\times10^{-6}]$		[40(10)]
k_5	(NH_3)	$1.56(15)\times10^{-7}$	97.5(17)	−48.2(49)
	(en)	$2.30(10)\times10^{-7}$	107(2)	−12(6)
k_{-3}	(NH_3)	$6.1(14)\times10^{-13}$	102.4(34)	−135.4(10)
	(en)	$2.47(5)\times10^{-13}$	120(6)	−86(21)
	–	$[1.24(3)\times10^{-13}]$		[−92(21)]
k_{-4}	(NH_3)	$2.7(6)\times10^{-8}$	102.3(35)	−47.0(97)
	(en)	$2.96(59)\times10^{-8}$	114(6)	−7(19)
k_{-5}	(NH_3)	$1.09(16)\times10^{-5}$	85.8(23)	−52.1(66)
	(en)	$3.3(6)\times10^{-5}$	90(4)	−27(11)
	–	$[1.65(3)\times10^{-5}]$		[−33(11)]

[a] The parameters for the ammine system are defined as shown in Scheme 1. The parameters for the 1,2-ethanediamine complexes are defined as shown in the Appendix. For this system the values for k_3, k_4 and k_5 have been taken from Ref. 3 (note that k_4 is for the cleavage of *one* Rh–O bond), and the other parameters have been calculated using published data as discussed in the text. Statistically corrected values, given in square brackets, have been calculated as shown in the Appendix.

nuclear species was studied spectrophotometrically at five temperatures (25.0, 40.0, 60.0, 80.0 and 100.0 °C), and the hydrogen ion concentration was varied from 10^{-7} to 1.0 M (see Experimental). The visible–ultraviolet spectra of the final product solutions were compared with the spectra of solutions of *cis*-$[Rh(NH_3)(H_2O)(OH)]S_{-2}O_6$ in 1 M $(Na,H)ClO_4$ with the same $[H^+]$. For solutions with $[H^+] = 5\times10^{-3}$–1.0 M, it could be concluded that hydrolysis to mononuclear species is quantitative. For solutions with $[H^+] = 10^{-7}$ M (1 M $NaClO_4$), the spectra also indicated quantitative formation of the mononuclear species, but only when the complex concentration was low (87 % completion at 60 °C and 94 % completion at 100 °C for $C_{Rh} = 1.8\times10^{-3}$ M, see above). In order to eliminate influence from the back-reaction (k_{-5}), values of k_{obs} for 1 M $NaClO_4$ were calculated on the basis of absorbances measured only during the first part of the reaction (two half-lives), and the spectrum of *cis*-$[Rh(NH_3)_4(H_2O)(OH)](ClO_4)_2$ in 1 M $NaClO_4$ was defined as the product spectrum and included the calculations.

The observed rate constants vary with $[H^+]$, as shown in Fig. 3. The $[H^+]$ dependence is consistent with Scheme 1. The equilibration between the binuclear species is more than 400 times faster than the cleavage of the monohydroxo-bridged species over the entire $[H^+]$ region, and it therefore follows that the monohydroxo-bridged species are in equilibrium with the dihydroxo-bridged species throughout the entire reaction. This leads to the expression shown in eqn. (3).

$$k_{calc} = \frac{(k_3/K_{a3})[H^+]^2 + k_4[H^+] + k_5K_{a1}{}^{d}}{[H^+] + K_{a1}{}^{d}/K_1 + K_{a1}{}^{d}} \qquad (3)$$

The parameters for k_3/K_{a3}, k_4 and k_5 were then determined by non-linear least-squares calculations using the known thermodynamic parameters for K_1 and $K_{a1}{}^{d}$. It is noted that there is satisfactory agreement between observed and calculated rate constants (Fig. 3), and that all parameters are well defined (Table 4). The rate constants for the condensation reaction k_{-3}, k_{-4} and k_{-5} were then calculated as described in the Appendix.

The rate constants k_{-3}, k_{-4} and k_{-5} for the corresponding 1,2-ethanediamine system have been calculated from published data[3,4] as shown in the Appendix, and are given in Table 4.

Discussion

The reaction scheme for the present ammine system shown in Scheme 1 is identical with that previously proposed for the 1,2-ethanediamine system.[3] The kinetic and thermodynamic data (with few exceptions discussed below) for the two systems are very similar, as seen in Tables 3 and 4. Most of the comments given previously in connection with the 1,2-ethanediamine system are therefore also relevant for the present study and will be mentioned only briefly here.

A significant difference between the two systems is that $\Delta H^‡(k_5)$ and in particular $\Delta S^‡(k_5)$ for the ammine system are smaller than those of the 1,2-ethanediamine system. Following our recent discussions[2] it seems reasonable to explain this difference in terms of a different degree of hydrogen-bond stabilization of the aquahydroxo species *cis,cis*-$(HO)(NH_3)_4Rh(OH)Rh(NH_3)_4(H_2O)^{4+}$. In Scheme 2 it is shown how the aqua hydroxo species may exist in two forms, one of which is stabilized by an intramolecular hydrogen bond. The existence of the latter conformation in

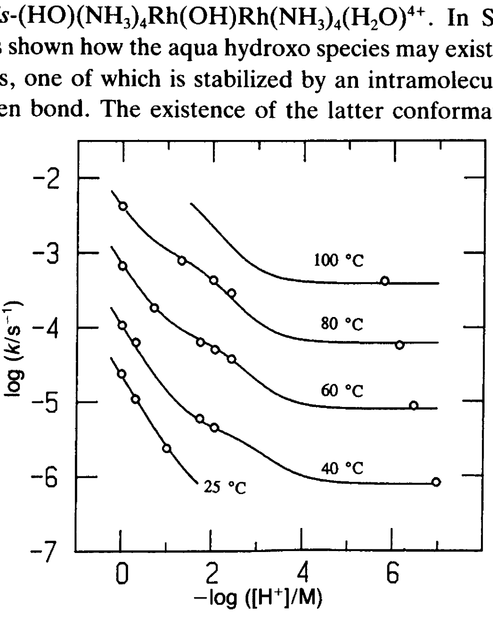
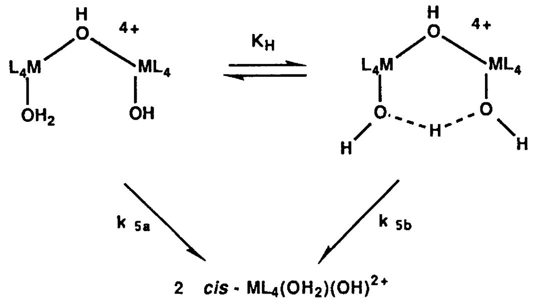


Fig. 3. Observed and calculated (solid line) rate constants for the equilibrium reaction.



Scheme 2. The monohydroxo-bridged aquahydroxo species may exist in two configurations, and it is proposed that the intramolecular hydrogen-bonded form is significantly more stable kinetically than is the other configuration.

the solid phase has been established by a crystal structure of the 1,2-ethanediamine iridium(III) analogue,[8] and its existence as the dominant form in aqueous solution has been shown unambigously on the basis of variations in the acid strength of a series of mono- and binuclear species.[2] For the present systems the values $K_H(NH_3) = 250$ and $K_H(en) = 1260$ have been estimated.[2] It follows that the observed rate constant for the cleavage may be expressed as the sum of the rate constants for cleavage of the two species in Scheme 2, which for $K_H \gg 1$ gives eqn. (4).

$$k_5 = k_{5a}/K_H + k_{5b} \tag{4}$$

As pointed out previously, the influence of this stabilization on the kinetics depends on the transition-state structure, i.e. whether the intramolecular hydrogen-bond is broken or not prior to the formation of the transition state. It was previously shown that the kinetic data for the 1,2-ethanediamine system support the former mechanism, which in terms of Scheme 2 corresponds to $k_{5a}/K_H \gg k_{5b}$. This leads to the approximative expression eqn. (5), and

$$k_5 = k_{5a}/K_H \tag{5}$$

using the known values for K_H, the rate constants for cleavage of the non-hydrogen-bond stabilized species may then be calculated: $k_{5a}(NH_3) = 3.9\times10^{-5}\ s^{-1}$ and $k_{5a}(en) = 2.9\times10^{-4}\ s^{-1}$. Since the rate constant k_4 also refers to cleavage of species which are not hydrogen bond stabilized, it seems reasonable to expect the two ratios $k_{5a}(en)/k_{5a}(NH_3) = 6$ and $k_4(en)/k_4(NH_3) = 10$ to be similar. This is seen to be the case. This result seems to support our earlier proposal[3] that the transition-state structure does not (to any large extent) involve a hydrogen bond between Rh–OH and Rh–OH_2. This is in conflict with a proposal[9] that dimerization involves, as a reactive species, hydrogen-bonded pairs of mononuclear cations. The formation of the latter species may be important in some systems, but will in those cases stabilize the mononuclear species, thermodynamically as well as kinetically.

Following the discussion above, it seems reasonable to expect that the ratios $k_3(en)/k_3(NH_3)$ and $k_4(en)/k_4(NH_3)$ are similar. This assumption makes it possible to estimate that $K_{a3}(en)/K_{a3}(NH_3) = 6$. This is in keeping with estimates of the relative acidities of the aqua bridge in a series of ammine and 1,2-ethanediamine *di*bridged species of chromium(III), rhodium(III) and iridium(III), obtained by the same kind of arguments.[2]

The rate constants for the condensation reactions vary in a similar way for the two systems. The roughly estimated values given recently for the amine system (25 °C) are similar to the more correct values given here, so the previous comments on the amine system[3] are valid for both systems, and will not be discussed here. The activation parameters for the amine system have not been given before and may now be compared with those for the ammine system. It is seen that both the enthalpy and the entropy of activation are smaller for the ammine system than for the amine system. The difference in entropy of activation is in agreement with the expected decrease in solvation on going from amine to ammine complexes.

The variation of the equilibrium constants K_3–K_6 is nearly the same for the ammine and the amine systems, and as pointed out previously,[3] the significant stabilization of the 4+ charged monohydroxo-bridged species is explained in terms of the intramolecular hydrogen bond. [The observed order is $K_4 \gg K_5 < K_6$ in contrast to the expected (on the basis of charge considerations alone) order $K_4 > K_5 > K_6$.]

Conclusions

It is concluded that the present new data for the ammine system show trends which are parallel to those obtained for the amine system, thereby supporting the mechanistic and thermodynamic results presented earlier. In addition the new data have now made it possible to study the variation imposed by changing the non-bridging ligands, and this has added new evidence in favour of earlier proposals. The reactions between the mono- and binuclear species can be understood fairly well in terms of the properties known from the substitution chemistry of the mononuclear species and properties which are due to the interactions between the two metal centres. Of the latter type, intramolecular hydrogen-bond formation is of particular importance, as also found for the reactions between monohydroxo- and dihydroxo-bridged species. Strong evidence points to the proposals that this type of interaction tends to stabilize the binuclear species, not only thermodynamically, but also kinetically.

Appendix

In the present ammine system the equilibrium constants K_3–K_5 and their respective rate constants are defined as shown in Scheme 1. K_6 is defined in eqn. (2) above. The constants K_3/K_{a3}, K_4 and K_6 were calculated using eqns. (6)–(9).

$$K_3/K_{a3} = (k_3/K_{a3})/k_{-3} = K_{a1}{}^{d}K_5/(K_{a1}{}^{m})^2 \tag{6}$$

$$K_4 = k_4/k_{-4} = K_{a1}{}^{d}K_5/K_{a1}{}^{m} \qquad (7)$$

$$K_5 = k_5/k_{-5} \qquad (8)$$

$$K_6 = k_{a2}{}^{m}K_5/K_{a2}{}^{d} \qquad (9)$$

In eqn. (9) $K_{a2}{}^{m}$ is the acid dissociation constant of *cis*-$Rh(NH_3)_4(H_2O)(OH)^{2+}$ and $K_{a2}{}^{d}$ is the acid dissociation constant of $(H_2O)(NH_3)_4Rh(NH_3)_4(OH)^{4+}$. The rate constants for the condensation reactions were then calculated from the known constants for the cleavage reactions using eqns. (6)–(9).

In the following we discuss the definitions of the constants for the 1,2-ethanediamine system and use the abbreviations for the different species as illustrated below:

Δ,Λ-dimer^{4+} = Δ,Λ-$(HO)(en)_2Rh(OH)Rh(en)(OH)_2{}^{4+}$

Δ-monomer^{4+} = *cis*-Δ-$Rh(en)_2(OH)(OH_2)^{2+}$

monomer^{4+} = Δ-monomer^{4+} + Λ-monomer^{4+}
(equimolar amounts)

One way to define the constants for *meso*-Δ,Λ-1,2-ethanediamine system is shown in eqns. (10)–(13). These definitions are similar to the definitions for the present ammine system and were used in our first study of the amine system.

$$K_3'/K_{a3} = (k_3'/K_{a3})/k_{-3}' = \frac{[\text{monomer}^{3+}]^2}{[\Delta,\Lambda\text{-dimer}^{5+}][\text{H}^+]} \qquad (10)$$

$$K_4' = k_4'/k_{-4}' = \frac{[\text{monomer}^{3+}][\text{monomer}^{2+}]}{[\Delta,\Lambda\text{-dimer}^{5+}]} \qquad (11)$$

$$K_5' = k_5'/k_{-5}' = \frac{[\text{monomer}^{2+}]^2}{[\Delta,\Lambda\text{-dimer}^{4+}]} \qquad (12)$$

$$K_6' = \frac{[\text{monomer}^{2+}][\text{monomer}^{+}]}{[\Delta,\Lambda\text{-dimer}^{3+}]} \qquad (13)$$

These constants, however, are valid only for solutions in which the amount of Δ- and Λ-isomers of the mononuclear species are equal, and only their sum is considered. More general definitions refer to the actual concentrations of the individual species and are given in eqns. (14)–(17).

$$K_3/K_{a3} = (k_3/K_{a3})/k_{-3} = \frac{[\Delta\text{-monomer}^{3+}][\Lambda\text{-monomer}^{3+}]}{[\Delta,\Lambda\text{-dimer}^{5+}][\text{H}^+]} \qquad (14)$$

$$\begin{aligned} K_4 = k_4/k_{-4} &= \frac{[\Delta\text{-monomer}^{3+}][\Lambda\text{-monomer}^{2+}]}{[\Delta,\Lambda\text{-dimer}^{5+}]} \\ &= \frac{[\Delta\text{-monomer}^{2+}][\Lambda\text{-monomer}^{3+}]}{[\Delta,\Lambda\text{-dimer}^{5+}]} \end{aligned} \qquad (15)$$

$$K_5 = k_5/k_{-5} = \frac{[\Delta\text{-monomer}^{2+}][\Lambda\text{-monomer}^{2+}]}{[\Delta,\Lambda\text{-dimer}^{4+}]} \qquad (16)$$

$$\begin{aligned} K_6 &= \frac{[\Delta\text{-monomer}^{2+}][\Lambda\text{-monomer}^{+}]}{[\Delta,\Lambda\text{-dimer}^{3+}]} \\ &= \frac{[\Delta\text{-monomer}^{+}][\Lambda\text{-monomer}^{2+}]}{[\Delta,\Lambda\text{-dimer}^{3+}]} \end{aligned} \qquad (17)$$

It should be noted that k_4 is the microscopic rate constant for the cleavage of *one* particular Rh–O bond, while k_3 and k_5 correspond to the cleavage of one of the two Rh–O bonds. Likewise, k_{-4} is the microscopic rate constant for the formation of the binuclear species from one of the two different enantiomeric pairs of mononuclear species. The constants for the 1,2-ethanediamine system given in Tables 3 and 4 were calculated from published data as follows. The value for K_5 is equal to $1/K_d(\Delta,\Lambda)$ taken from Ref. 4, and the other equilibrium constants were then calculated using eqns. (14)–(17). The rate constants k_3/K_{a3} and k_5 are equal to the respective values in Ref. 3, while k_4 is equal to $\frac{1}{2}$ k_4 in Ref. 3. The constants k_{-3}–k_{-5} were then calculated using eqns. (14)–(17).

When comparing these constants with those of, e.g., the ammine system, one has to make a statistical correction, owing to the fact that in the amine system, condensation may also lead to racemic isomers (see also below). The relations between the three sets of constants for the *meso*-1,2-ethanediamine system are given by eqns. (18)–(24).

$$K_i = \tfrac{1}{4}K_i' = \tfrac{1}{2}K_i^{\text{stat}},\ i = 3\text{–}6 \qquad (18)$$

$$k_3 = k_3' = k_3^{\text{stat}} \qquad (19)$$

$$k_4 = \tfrac{1}{2}k_4' = \tfrac{1}{2}k_4^{\text{stat}} \qquad (20)$$

$$k_5 = k_5' = k_5^{\text{stat}} \qquad (21)$$

$$k_{-3} = 4k_{-3}' = 2k_{-3}^{\text{stat}} \qquad (22)$$

$$k_{-4} = 2k_{-4}' = k_{-4}^{\text{stat}} \qquad (23)$$

$$k_{-5} = 4k_{-5}' = 2k_{-5}^{\text{stat}} \qquad (24)$$

For the corresponding racemic binuclear species (Δ,Δ and Λ,Λ), the equilibrium and rate constants K_i, k_i' and k_{-i}' are defined as shown above in eqns. (10)–(13), but now Δ,Δ-dimer^{z+} means the *sum* of the corresponding Δ,Δ- and Λ,Λ-isomers.

The constants K_i, k_i and k_{-i} for the Δ,Δ-isomers are defined as shown in eqns. (25)–(28), and similar equations may be written for the Λ,Λ isomers.

$$K_3/K_{a3} = (k_3/K_{a3})/k_{-3} = \frac{[\Delta\text{-monomer}^{3+}]^2}{[\Delta,\Delta\text{-dimer}^{5+}][\mathrm{H}^+]} \quad (25)$$

$$K_4 = k_4/k_{-4} = \frac{[\Delta\text{-monomer}^{3+}][\Delta\text{-monomer}^{2+}]}{[\Delta,\Delta\text{-dimer}^{5+}]} \quad (26)$$

$$K_5 = k_5/k_{-5} = \frac{[\Delta\text{-monomer}^{2+}]^2}{[\Delta,\Delta\text{-dimer}^{4+}]} \quad (27)$$

$$K_6 = \frac{[\Delta\text{-monomer}^{2+}][\Delta\text{-monomer}^{+}]}{[\Delta,\Delta\text{-dimer}^{3+}]} \quad (28)$$

The relation between these constants and the statistically corrected constants are given by eqns. (29)–(31).

$$K_i = \tfrac{1}{2}K_i' = K_i^{\text{stat}} \quad (29)$$

$$k_i = k_i' = k_i^{\text{stat}} \quad (30)$$

$$k_{-i} = 2k_{-i}' = k_{-i}^{\text{stat}},\ i = 3\text{–}6 \quad (31)$$

Acknowledgement. Financial support by the Carlsberg Foundation and the Danish Natural Research Council is gratefully acknowledged. The author is indebted to Johnson Matthey & Co. for the loan of rhodium(III) chloride hydrate. Dr. Peter Andersen is thanked for valuable discussions.

References

1. Baes, C. F. and Mesmer, R. E. *Hydrolsis of Cations,* Wiley, New York 1976.
2. Springborg, J. In: A. G. Sykes, Ed., *Advances in Inorganic Chemistry,* Academic Press, San Diego 1988, Vol. 32, p. 55.
3. Kaas, K. and Springborg, J. *Inorg. Chem. 26* (1987) 387.
4. Bjerrum, M., Kaas, K., Larsen, E., Nielsen, B. and Springborg, J. *Inorg. Chem. 28* (1989) 532.
5. Christensson, F. and Springborg, J. *Inorg. Chem. 24* (1985) 2129.
6. Hancock, P. M., Nielsen, B. and Springborg, J. *Inorg. Synth. 24* (1986) 220.
7. Hancock, P. M. and Skibsted, L. H. *Acta Chem. Scand., Ser. A 38* (1984) 87.
8. Galsbøl, F., Larsen, S., Rasmussen, B. and Springborg, J. *Inorg. Chem. 25* (1986) 290.
9. Ardon, M. and Bino, A. *Struct. Bond. 65* (1987) 1.
10. Skibsted, L. H. *Acta Chem. Scand., Ser. A 40* (1986) 364.
11. Hancock, P. M., Nielsen, B. and Springborg, J. *Acta Chem. Scand., Ser. A 36* (1982) 313.

Received January 27, 1992.