

Steric Effects on Water-Exchange Mechanisms of Aquapentakis(amine)metal(III) Complexes (Metal = Chromium, Cobalt, Rhodium). A Variable-Pressure Oxygen-17 NMR Study^{1–3}

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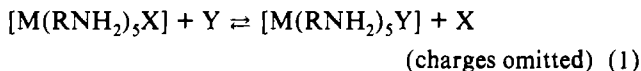
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The water-exchange rate constants and activation parameters for the $[M(\text{CH}_3\text{NH}_2)_5\text{H}_2\text{O}]^{3+}$ ($M = \text{Cr}(\text{III}), \text{Co}(\text{III}), \text{Rh}(\text{III})$) complexes, determined by variable-temperature and -pressure ^{17}O NMR are respectively as follows: $k_{\text{ex}}^{298} = (4.1 \pm 0.5) \times 10^{-6}$, $(700 \pm 80) \times 10^{-6}$, and $(10.6 \pm 0.6) \times 10^{-6} \text{ s}^{-1}$; $\Delta H^\ddagger = 98.5 \pm 3$, 99.0 ± 6 , and $112.7 \pm 2 \text{ kJ mol}^{-1}$; $\Delta S^\ddagger = -17.5 \pm 10$, $+26.7 \pm 22$, and $+37.8 \pm 6 \text{ J K}^{-1} \text{ mol}^{-1}$; $\Delta V^\ddagger = -3.8 \pm 0.3$, $+5.7 \pm 0.2$, and $+1.2 \pm 1.1 \text{ cm}^3 \text{ mol}^{-1}$. These results indicate a clear differentiation in the intimate substitution mechanism operating for these complexes. For the Cr(III) complex, a clearly associative activation mode operates, and for the Co(III) analog, a clearly dissociative activation mode operates, while the borderline nature of the Rh(III) complex is quantified by an activation volume value practically zero. The differences in the values obtained for ΔV^\ddagger and for k_{ex}^{298} as compared with those corresponding to the analogous $[M(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ complexes are interpreted in view of a shift to more dissociatively (or less associatively) activated mechanisms operating for the complexes with larger amine groups. That is, the increase in the steric congestion around the metal center causes the mechanism to be shifted to the dissociatively activated side of the $I_a \leftrightarrow I_d$ mechanistic continuum.

Introduction

The nature of the steric effects on the substitution reactions of aquapentakis(amine)metal(III) complexes has attracted much attention, both historically⁵ and recently.⁶ The mechanisms of their substitution reactions (eq 1) have always been considered

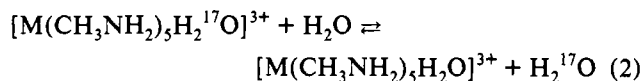


as falling strictly into the Langford–Gray I_a or I_d category. This assumption has led to important controversies between the different groups studying the substitution reaction mechanisms of these types of complexes.⁷ When one considers the full $A \leftrightarrow I \leftrightarrow D$ mechanistic span as a continuum,⁸ the possibility of the existence of some factors inducing a shift in the mechanism can be considered.

The use of high-pressure techniques⁹ has enabled the obtention of an important amount of ΔV^\ddagger values for the water-exchange

reactions of $[M(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ complexes.¹⁰ In these reactions, the problems arising from the consideration of the solvational terms involved in unsymmetrical reactions are omitted and the full interpretation of an activation volume for a symmetrical reaction with no charge redistribution can be achieved. That is, these values are not influenced by the typical electrostriction or solvational terms¹¹ and can be easily considered as intrinsic values for the reaction. By doing so, one can assess the degree of associativity or dissociativity of a reaction.

In this paper, we present the study of water exchange for aquapentakis(methylamine)metal(III) complexes (eq 2) for $M = \text{Cr}, \text{Co},$ and Rh as a function of temperature and pressure. The



data obtained allow us to establish, independently of the nature of the operating reaction mechanism, the existence of a dissociative shift in the reaction mechanism induced by the steric demands of the inert skeleton of the metal complex.

Experimental Section

Chemicals. Trifluoromethanesulfonic acid ($\text{CF}_3\text{SO}_3\text{H}$, 99%, Aldrich) (triflic acid or HTrifl) and ^{17}O -enriched water (10 atom %, normalized in ^1H , Yeda) were used as received. Sodium triflate ($\text{CF}_3\text{SO}_3\text{Na}$) was prepared by reaction of the corresponding acid and sodium hydroxide (Merck, p.a.) and recrystallized three times in water.

Preparation of the $[M(\text{CH}_3\text{NH}_2)_5\text{H}_2\text{O}](\text{Trifl})_3$ Complexes. All aquapentakis(methylamine)metal(III) complexes were prepared according to the procedure published by Lawrance.⁶ $[M(\text{CH}_3\text{NH}_2)_5\text{Trifl}](\text{Trifl})_2$ were produced by dissolution of the corresponding chloro complexes¹² in anhydrous triflic acid with a N_2 purge to eliminate the HCl formed; recrystallization in an aqueous 0.1 M HTrifl solution gives the desired final complexes. Anal. Calcd (found, before enrichment) for $[\text{Cr}$

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Table 1. Water-Exchange Rate Constants of $[M(\text{CH}_3\text{NH}_2)_5\text{H}_2\text{O}]^{3+}$ ($M = \text{Cr(III), Co(III), Rh(III)}$), k_{ex} , as a Function of Temperature^a

$[\text{Cr}(\text{CH}_3\text{NH}_2)_5\text{H}_2\text{O}]^{3+}$		$[\text{Co}(\text{CH}_3\text{NH}_2)_5\text{H}_2\text{O}]^{3+}$		$[\text{Rh}(\text{CH}_3\text{NH}_2)_5\text{H}_2\text{O}]^{3+}$	
T/K	$10^6 k_{\text{ex}}/\text{s}^{-1}$	T/K	$10^6 k_{\text{ex}}/\text{s}^{-1}$	T/K	$10^6 k_{\text{ex}}/\text{s}^{-1}$
301.3	7 ± 1^b	277.2	24 ± 1	285.6	1.1 ± 0.2
313.1	26 ± 1^c	283.0	100 ± 2^d	291.8	4.5 ± 0.2
313.5	34 ± 3	294.0	415 ± 24^d	297.2	9.4 ± 0.1
324.7	114 ± 2	300.7	1220 ± 90	303.2	22.2 ± 0.2^d
328.6	159 ± 7	305.7	1770 ± 400	309.4	64.8 ± 0.4
332.8	261 ± 5	312.6	4000 ± 900	314.7	137 ± 4^d
350.5	2130 ± 250			317.5	169 ± 3
				327.3	630 ± 20
				334.6	1810 ± 40
				350.3	9800 ± 400

^a [complex] = 0.100 *m*, [H⁺] = 0.100 *m* (HTrifl), ionic strength $\mu = 0.70$ *m* (NaTrifl). ^b [H⁺] = 0.050 *m*. ^c [H⁺] = 0.075 *m*. ^d [H⁺] = 0.025 *m*.

$(\text{CH}_3\text{NH}_2)_5\text{H}_2\text{O}(\text{Trifl})_3$: C, 14.28 (14.29); H, 4.05 (3.94); N, 10.41 (10.61). For the Co(III) and Rh(III) complexes, purities before enrichment were controlled by UV-vis spectroscopy.^{6b,13} Dissolution of the complexes in 10% ¹⁷O-enriched water, followed by equilibration (4 days at 25 °C for Cr(III), 12 h at 40 °C for Co(III), and 12 h at 80 °C for Rh(III)) of the solutions, yields, after evaporation at reduced pressure and low temperature, the desired H₂¹⁷O enriched complexes. After enrichment, the purity of the three aquapentakis(methylamine)metal(III) complexes was checked by UV-vis spectroscopy.

NMR Measurements. All the samples for the NMR measurements were prepared by weight, and the concentrations were calculated as molalities. Solutions contained a known weight of HTrifl (and sometimes NaTrifl) to adjust acidity and ionic strength. All ¹⁷O NMR spectra were recorded on a Bruker AM-400 spectrometer equipped with a 9.4-T wide-bore cryomagnet operating at 54.24 MHz. Variable-temperature kinetic measurements were performed, using 10 mm o.d. sample tubes. Thermostating of the samples was achieved with a Bruker BVT-2000 unit. The temperatures (± 0.5 K) were measured before and after spectral accumulation by substituting the sample with a calibrated platinum resistor.¹⁴ A total of 4096 points were recorded, resulting from 1000–10 000 scans using a frequency window of 10–30 kHz. Variable-pressure experiments were carried out with a homebuilt probehead,¹⁵ using the variable-temperature acquisition parameters.

Results

Variable-Temperature Kinetics. For the cobalt and rhodium aquapentakis(methylamine)metal(III) complexes the water-exchange reaction (eq 2) was followed by monitoring the depletion of the aqua ion and the enrichment of bulk water in oxygen-17 with time. The resonance due to the bound water was at -93 ppm for Co(III) and -88 ppm for Rh(III) (reference to the bulk water signal). As an example, for the Rh(III) complex, at 297.2 K, the transverse relaxation rates, $1/T_2$, of quadrupolar origin obtained by line-width measurements, are 2140 s⁻¹ for coordinated and 530 s⁻¹ for bulk water signal. The exchange reactions were allowed to proceed to equilibrium. The time dependence of the mole fraction of labeled water coordinated to the metal center, x , obtained by integration of the two signals was fitted to eq 3 with

$$x = x_{\infty} + (x_0 - x_{\infty}) \exp\left(-\frac{k_{\text{ex}}t}{1 - x_{\infty}}\right) \quad (3)$$

$x_{\infty} \approx [\text{bound water}]/55.5 < 1 \times 10^{-2}$. The adjustable parameters were k_{ex} , the rate constant for the exchange of bound water, and x_0 . The exchanges were followed directly in the probeheads at a series of temperatures between 277 and 312 K for the cobalt complex and between 285 and 350 K for the rhodium one. The water-exchange rate constants obtained in this way (Table 1), were least-squares-fitted to eq 4, leading to $k_{\text{ex}}^{298} = (700 \pm 80) \times 10^{-6} \text{ s}^{-1}$, $\Delta H^{\ddagger} = 99.0 \pm 6 \text{ kJ mol}^{-1}$, $\Delta S^{\ddagger} = +26.7 \pm 22 \text{ J K}^{-1} \text{ mol}^{-1}$ for Co(III) and $k_{\text{ex}}^{298} = (10.6 \pm 1) \times 10^{-6} \text{ s}^{-1}$, $\Delta H^{\ddagger} = 112.7 \pm 2 \text{ kJ mol}^{-1}$, $\Delta S^{\ddagger} = +37.8 \pm 6 \text{ J K}^{-1} \text{ mol}^{-1}$ for Rh(III).

$$k_{\text{ex}} = \frac{k_{\text{B}}T}{h} \exp\left(\frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT}\right) \quad (4)$$

For the paramagnetic t_{2g}^3 chromium(III) complex, only the free-water signal could be observed, preventing the use of the mole fraction of bound water, x . Instead, the increase in height, h , of the free signal was used in the fitting procedure. In some cases the surfaces as obtained from Lorentzian least-squares fitting were used, leading to the same rate constants within experimental errors. Its time dependence, directly derived from eq 3, is given by eq 5. The only drawback of this procedure is the need to fit

$$h_{\text{free}} = h_{\text{free}}^{\infty} + (h_{\text{free}}^0 - h_{\text{free}}^{\infty}) \exp\left(-\frac{k_{\text{ex}}t}{1 - x_{\infty}}\right) \quad (5)$$

now three parameters, k_{ex} , h_{free}^0 , and h_{free}^{∞} , instead of two. For the chromium complex, the variable-temperature runs were performed between 301 and 350 K (Table 1). At higher temperatures decomposition occurred. The rate constant and the activation parameters obtained are the following: $k_{\text{ex}}^{298} = (4.1 \pm 0.5) \times 10^{-6} \text{ s}^{-1}$, $\Delta H^{\ddagger} = 98.5 \pm 3 \text{ kJ mol}^{-1}$, $\Delta S^{\ddagger} = -17.5 \pm 10 \text{ J K}^{-1} \text{ mol}^{-1}$.

Variable-Pressure Kinetics. Variable-pressure kinetic runs were carried out at 288.5 K for the Co(III) (eq 5), 318.3 K for the Rh(III) (eq 4), and 333.3 K for the Cr(III) complex (eq 5) up to 200 MPa and analyzed with the equations given in the parentheses. The pressure dependence of the exchange rate constant, k_{ex} , is usually assumed to be a quadratic function of the pressure P (eq 6). In this equation, $k_{\text{ex},0}$ is the exchange rate

$$\ln k_{\text{ex}} = \ln k_{\text{ex},0} - \frac{(\Delta V^{\ddagger})P}{RT} + \frac{(\Delta\beta^{\ddagger})P^2}{2RT} \quad (6)$$

constant at zero pressure and temperature T , ΔV^{\ddagger} is the activation volume of the reaction at zero pressure, and $\Delta\beta^{\ddagger}$ is the compressibility coefficient of activation. Very often the deviation from linear behavior is well within experimental error, and $\Delta\beta^{\ddagger}$ is therefore set to zero.^{11a} The results obtained are $\Delta V^{\ddagger} = +5.7 \pm 0.2 \text{ cm}^3 \text{ mol}^{-1}$, $k_0^{288.5} = (1.9 \pm 0.1) \times 10^{-4} \text{ s}^{-1}$ for Co(III), $\Delta V^{\ddagger} = +1.2 \pm 1.1 \text{ cm}^3 \text{ mol}^{-1}$, $k_0^{318.3} = (2.2 \pm 0.1) \times 10^{-4} \text{ s}^{-1}$ for Rh(III), and $\Delta V^{\ddagger} = -3.8 \pm 0.3 \text{ cm}^3 \text{ mol}^{-1}$, $k_0^{333.3} = (1.7 \pm 0.1) \times 10^{-4} \text{ s}^{-1}$ for Cr(III). The experimental and calculated rate constants, k_{ex} , normalized to the exchange rate constants $k_{\text{ex},0}$ (at atmospheric pressure), are shown in Figure 1. The complex concentrations were approximately the same (~ 0.1 *m*), except for that of the Co(III) complex (~ 0.2 *m*), as in the variable-temperature measurements.

Discussion

From the results collected in Table 2 it is clear that, for both

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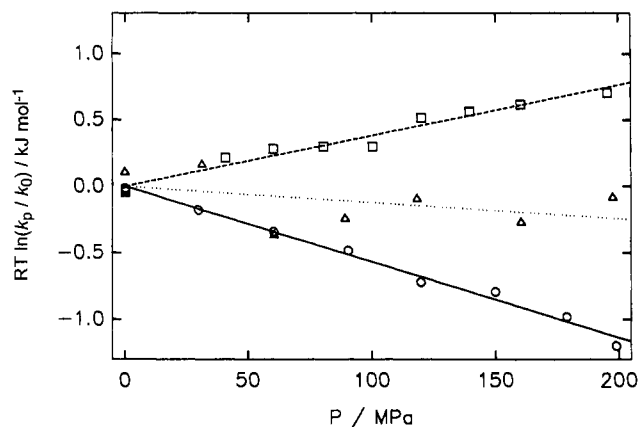


Figure 1. Effect of pressure on the water-exchange rate constant k_p/s^{-1} for $[M(\text{CH}_3\text{NH}_2)_5\text{H}_2\text{O}]^{3+}$ ($M = \text{Cr(III)}, \text{Co(III)}, \text{Rh(III)}$) in aqueous solutions: (\square) Cr(III), 333.3 K, [complex] = 0.100 *m*; (\circ) Co(III), 288.5 K, [complex] = 0.200 *m*; (\triangle) Rh(III), 318.3 K, [complex] = 0.100 *m*. $[\text{H}^+] = 0.100$ *m* (HTrifl); ionic strength $\mu = 0.70$ *m* for Cr(III) and Rh(III) and 1.30 *m* for Co(III).

Cobalt and chromium $[M(\text{RNH}_2)_5\text{H}_2\text{O}]^{3+}$ complexes, an important difference in the reaction rate constants for the water exchange k_{ex}^{298} exists on going from $R = \text{H}$ to $R = \text{CH}_3$, while for the rhodium(III) complex only a slight increase is obtained. This would indicate that for the $[\text{Co}(\text{RNH}_2)_5\text{H}_2\text{O}]^{3+}$ complex the reaction mechanism for the water exchange is dissociatively activated, while for the $[\text{Cr}(\text{RNH}_2)_5\text{H}_2\text{O}]^{3+}$ complex the same reaction is intrinsically associatively activated. For the analogous rhodium(III) compound the difference is not important enough to allow us to give any interpretation about the nature of the intimate mechanism. The conclusion that can be drawn from the trends in the values of the activation volumes is much more important. In all cases an important increase in ΔV^\ddagger is observed for all the complexes on increasing the steric demands of the inert skeleton. This indicates that for all the $[M(\text{RNH}_2)_5\text{H}_2\text{O}]^{3+}$ systems studied the effect produced by the increase of the bulkiness of the R substituents is simply that of a decrease of the associativeness, or increase in dissociativeness, of the reaction mechanism for the water exchange, independently of its intimate nature.^{6c}

In this study it is made clear that the steric hindrance of the molecule as a whole is of great importance in shifting the intimate mechanism of a given reaction. As in the case of the $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ (I_a mechanism) and $[\text{Mn}(\text{DMF})_6]^{2+}$ (I_d mechanism) complexes,^{9c} the consequence of the steric increase of the inert skeleton of the $[M(\text{RNH}_2)_5\text{H}_2\text{O}]^{3+}$ complex is that of the increase of the dissociative character of the mechanism. For the Co(III) and Cr(III) pentakis(amine) centers no change is observed in the sign of the activation volume for the water exchange, while for the Rh(III) center the value increases to practically zero within experimental error.

Although it has been suggested that the value of ΔV^\ddagger cannot be quantitatively taken as a measure of the nature of the intimate mechanism operating for the water-exchange reactions on pentakis(amine) centers, due to possible differences in solvational and hydrogen-bonding interactions affecting the $\Delta V^\ddagger_{\text{sol}}$ term of the measured $\Delta V^\ddagger_{\text{exp}}$,^{7a} it is obvious that the qualitative interpretation of the available data is still correct.^{6d} The measure of ΔV^\ddagger for the solvent exchange in Mn^{2+} solvato complexes of H_2O and DMF clearly indicates a changeover from an associatively to a dissociatively activated interchange mechanism on increasing the steric demands of the coordinating solvent molecule.¹⁰ In our case from the k_{ex}^{298} and ΔV^\ddagger values obtained we can assume that for the $[M(\text{CH}_3\text{NH}_2)_5\text{H}_2\text{O}]^{3+}$ substitution reactions an associatively activated interchange mechanism is operating for the

Cr(III) complexes while the activation is dissociative for the Co(III) complexes. In both cases the increase of steric demands forces the intimate nature of the mechanism to have a more dissociative character, although there is no changeover in the mechanism.

These results are in good agreement with or are clarification of former controversy on interpretation of results reported for ligand substitution on similar $[M(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ complexes.²¹ The positive ΔV^\ddagger observed for water exchange on the cobalt(III) complex infers the operation of an I_d mechanism, while the negative value characterizing the chromium(III) complex suggests the operation of an I_a mechanism. This difference in sign of ΔV^\ddagger , and the implied mechanistic difference, has also been observed for the substitution of $L = \text{OSMe}_2, \text{OCHNH}_2, \text{OC}(\text{NH}_2)_2, \text{OC}(\text{NHMe})_2$, and OCMeNMe_2 and several other uncharged oxygen donor ligands by water in $[\text{Cr}(\text{NH}_3)_5\text{L}]^{3+}$ and $[\text{Co}(\text{NH}_3)_5\text{L}]^{3+}$.^{6d,22} Thus, there seems little doubt that there is a significant mechanistic difference for ligand substitution on the two metal centers. The aquation of $[M(\text{NH}_3)_5\text{L}]^{(3-x)+}$ has featured strongly in mechanistic debate.^{5f,7ab,8,9c,10,23,24} A linear free energy relationship (LFER) with a slope of unity exists between the logarithm of the aquation rate constant and that of the equilibrium stability constant for the formation of a series of $[\text{Co}(\text{NH}_3)_5\text{L}]^{3+}$ complexes.²⁵ A similar volume relationship $\delta\Delta V^\ddagger = \alpha(\delta\Delta V^\circ)$, with $\alpha = 1$, for the substitution on $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ by several anions has also been found. On these bases, the assignment of an I_d mechanism for ligand substitution on $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ is well justified. However, the mechanism of substitution of anionic ligands on $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ has received both I_d and I_a assignments by various authors. This dichotomy of viewpoint arises substantially because the negative ΔV^\ddagger for water exchange on $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ and a slope of 0.69 from a LFER²⁶ for the aquation of $[\text{Cr}(\text{NH}_3)_5\text{L}]^{3+}$ are consistent with I_a mechanisms but the small selectivity of $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ toward anation^{8a} has been taken as evidence for the operation of an I_d mechanism.^{27,28} The question is how to resolve these apparently conflicting mechanistic assignments. The replacement of five waters in $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ by NH_3 in $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ causes a 20-fold increase in the lability of the single remaining water (which is quite small by comparison with such replacement in $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$)^{29,30} and appears to decrease the importance of the a-activation mode in the approach to the transition state (see also above discussion of the change toward d-activation due to increased ligand size).³¹ Mechanistic interpretation now hinges on the degree to which a-activation needs to be dominant in an interchange mechanism before significant selectivity of the incoming ligand is apparent. It seems likely that a combination of the decreased importance of a-activation and the hardness of Cr^{3+} decreases selectivity to a low level and that in consequence this incoming ligand L competes poorly with the small hard base H_2O , which is present as the solvent in large excess concentration over competing L. If these suppositions are correct, the absence of selectivity is not a diagnostic of mechanism for $[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$, and the negative ΔV^\ddagger for water exchange remains as the most reliable indicator of mechanism. Although structural information could assist in understanding the observed ΔV^\ddagger trends,

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Table 2. Rate Constants and Activation Parameters for Water Exchange on Cr(III), Co(III), and Rh(III) Complexes

complex	$10^6 k_{ex}^{298}/s^{-1}$	$\Delta H^\ddagger/kJ\ mol^{-1}$	$\Delta S^\ddagger/J\ K^{-1}\ mol^{-1}$	$\Delta V^\ddagger/cm^3\ mol^{-1}$	ref
$[Cr(H_2O)_6]^{3+}$	2.4	108.6 ± 3	$+11.6 \pm 9$	-9.6 ± 0.1	16, 17
$[Cr(NH_3)_5H_2O]^{3+}$	60^a	97.1 ± 2	0.0 ± 7	-5.8 ± 0.2	18
$[Cr(CH_3NH_2)_5H_2O]^{3+}$	4.1 ± 0.5	98.5 ± 3	-17.5 ± 10	-3.8 ± 0.3	this work
$[Co(NH_3)_5H_2O]^{3+}$	5.7^a	111.3 ± 1	$+28 \pm 4$	$+1.2 \pm 0.2$	19
$[Co(CH_3NH_2)_5H_2O]^{3+}$	700 ± 80	99.0 ± 6	$+26.7 \pm 22$	$+5.7 \pm 0.2$	this work
$[Rh(H_2O)_6]^{3+}$	$(2.2 \pm 2.7) \times 10^{-3}$	131 ± 23	$+29 \pm 69$	-4.2 ± 0.6	20
$[Rh(NH_3)_5H_2O]^{3+}$	8.4^a	103.0 ± 1	$+3.3 \pm 5$	-4.1 ± 0.4	18
$[Rh(CH_3NH_2)_5H_2O]^{3+}$	10.6 ± 0.6	112.7 ± 2	$+37.8 \pm 6$	$+1.2 \pm 1.1$	this work

^a Calculated by using ΔH^\ddagger and ΔS^\ddagger values.

the only available data, for Co(III) complexes,^{6c} do not show any significant difference in the Co–OH₂ bond length on increasing the size of the R amine substituent, the steric hindrance being only evident in the molecule as a whole. Thermal activation parameters shown in Table 2 are less informative. ΔH^\ddagger values are very similar for all reactions and are similar to those obtained for other substitution reactions. As for the ΔS^\ddagger values, they are more scattered, although no definite trend is observed. Taking into account the errors involved in the ΔS^\ddagger determination, no meaningful discussion can be derived.

For the Rh(III) complexes a trend toward more positive ΔV^\ddagger values is also observed, but now the sign of ΔV^\ddagger changes from negative to slightly positive. Probably the more borderline nature of the substitution reactions of the pentakis(amine)rhodium(III) complexes is responsible for this effect.³²

In conclusion, the rate constants and the volumes of activation

for a series of water-exchange reactions on $[M(RNH_2)_5H_2O]^{3+}$ (R = H, CH₃) suggest an I_d mechanism for cobalt(III), an I_a mechanism for chromium(III), and probably a borderline I mechanism for rhodium(III).

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Supplementary Material Available: Water-exchange rate constants for $[M(CH_3NH_2)_5H_2O]^{3+}$ (M = Cr(III), Co(III), Rh(III)), k_{ex} , as a function of pressure (Table SI) (1 page). Ordering information is given on any current masthead page.

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