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Mechanism and Stereochemistry of the Water-Exchange Reaction on Aqua Pentaammine and Aqua Pentakis-Methylamine Rhodium(III) Ions

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The water-exchange reaction on $Rh(NH_3)_5OH_2^{3+}$ and $Rh(NH_2CH_3)_5OH_2^{3+}$ has been investigated by ab initio calculations on all stationary points of the potential energy surface (reactants/products, transition states, and intermediates, if there are any). The water-exchange on $Rh(NH_3)_5OH_2^{3+}$ proceeds via the I (interchange) mechanism, whereas that on $Rh(NH_2CH_3)_5OH_2^{3+}$ follows a dissociative (I_d or D) pathway because of the bulky NH_2CH_3 ligands. Both reactions proceed with retention of the configuration. For the ammonia complex, the computed activation energy agrees with experiment, whereas for the methylamine one, equal activation energies were found for the I_d and the D pathways, and they are lower than $\Delta H_{298}^{\ddagger}$ by 22 kJ/mol. The distinction of these two mechanisms is not possible on the basis of the present calculations, and the limitations of the model are discussed. The relation between the electronic structure of the transition state for the interchange mechanism and the intrinsic component of the activation volume is analyzed via the comparison of the water-exchange reactions on the aqua pentaammine complexes of Ru^{III} and Rh^{III}. For these two very similar exchange reactions, which give rise to equal experimental activation volumes ($\Delta V_{298}^{\ddagger}$), the intrinsic and electrostrictive components are most likely quite different.

Introduction

A few years ago, the structures of the transition states involved in the water-exchange reaction (eq 1) on di- and trivalent metal hexaaqua ions were investigated by ab initio quantum chemical methods.[1−4]

$$M(OH_2)_6^{n+} + \mathbf{H_2O} \rightarrow M(OH_2)_5\mathbf{OH_2}^{n+} + H_2O \qquad (1)$$

On the basis of these structures, the associative (A), associative interchange (I_a), or dissociative (D) mechanism could be attributed in a straightforward way to all computed exchange reactions. Although a rather simple gas-phase model[1] was used, in which dynamic electron correlation was neglected, it allowed the reproduction[1,2,4] of the experimental activation energies.[5]

Recently, the water-exchange on $V(OH_2)_6^{2+}$, $Mn(OH_2)_6^{2+}$, and $Fe(OH_2)_6^{2+}$ was reinvestigated[6] by taking into account electron correlation and hydration, whereby the surrounding solvent was treated as a dielectric continuum. This improved model[7] led to slightly more accurate activation energies than the calculations on free ions (in the gas phase). The model, with its limitations, was analyzed, and the electronic structure of the heptacoordinated species, which is either a transition state or an intermediate, was discussed. For all these investigated hexaaqua ions,[1,2,4,6] no transition state for the I_d mechanism has been found and possible reasons for that have been discussed.[2]

Transition states for the I_d mechanism have been found for the aquation of $Co(NH_3)_5Cl^{2+}$,[8] $Co(NH_3)_5SCN^{2+}$,[9] and $Co(NH_3)_5NCS^{2+}$,[9] or the corresponding anations of $Co(NH_3)_5OH_2^{3+}$. All these calculations on the pentaammine complexes of cobalt(III) were performed by taking into account hydration, but not dynamic electron correlation.

Pentaamine complexes of cobalt(III) and rhodium(III) are valence isoelectronic and both have a low-spin d_π^6 electron configuration.[10] Water-exchange on $Ru(NH_3)_5OH_2^{3+}$ (reaction 2), with one fewer $4d_\pi$ electron than the corresponding rhodium(III) compound, has been investigated recently with quantum chemical methods, and the effects of hydration and electron correlation were analyzed.[7]

$$Ru(NH_3)_5OH_2^{3+} + \mathbf{H_2O} \rightarrow Ru(NH_3)_5\mathbf{OH_2}^{3+} + H_2O \quad (2)$$

The experimental[11] volume of activation, $\Delta V_{298}^{\ddagger} = -4.0$ cm^3/mol, is moderately negative and suggests the I_a mechanism for reaction 2. According to the quantum chemical calculations,[7] the mechanism with the lowest activation energy is the I_a pathway that proceeds with retention of the configuration. The interchange mechanism involving the attack of the entering water opposite to the leaving water ligand would lead to stereomobility, but it requires a higher activation energy (by ∼33 kJ/mol).[7] The D mechanism, which would also proceed with retention of the configuration, would be more advantageous than the stereomobile pathway. It is, however, also unfavorable for the water-exchange on $Ru(NH_3)_5OH_2^{3+}$, because it requires a higher activation energy (15 kJ/mol) than the interchange mechanism with retention of the configuration. Because this energy difference is relatively small, the D mechanism might possibly become the most favorable one in complexes with bulky or chelating ligands.

The activation volumes for the water-exchange on $Ru(NH_3)_5OH_2^{3+}$ and $Rh(NH_3)_5OH_2^{3+}$ (reactions 2 and 3, respectively) are equal (namely, −4.0 and −4.1 cm^3/mol,[11,12] respectively), despite the disparate electronic structures of the two metal centers.

$$Rh(NH_3)_5OH_2^{3+} + \mathbf{H_2O} \rightarrow Rh(NH_3)_5\mathbf{OH_2}^{3+} + H_2O \quad (3)$$

In a heptacoordinated species of first-row transition metals, regardless of whether it is a transition state or an intermediate,

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TABLE 1: Calculated Total and Relative Energies, Experimental Activation Parameters, and Change of the Sum of the Rhodium(III)−Ligand Bond Lengths

Species	Basis set	E,[a] Hartrees	$\Delta E^\ddagger$ or ΔE, kJ/mol	$\Delta H_{298}^\ddagger/\Delta G_{298}^\ddagger$, kJ/mol	$\Delta\sum d(\text{Ru-L})$, Å	$\Delta V_{298}^\ddagger$, cm^3/mol
$Rh(NH_3)_5OH_2{\cdot}OH_2^{3+}$	A	−543.426005(20)	0.0		0.0	
[*cis*-$Rh(NH_3)_5{\cdots}(OH_2)_2^{3+}]^\ddagger$	A	−543.387339(175)	101.5	102.9 ± 1.3/102[b]	0.01	−4.1 ± 0.4[b]
$[Rh(NH_3)_5{\cdots}(OH_2)_2^{3+}]^{\ddagger}$ [c]	A	−543.339203(105)	227.9		0.58	
$Rh(NH_3)_5OH_2^{3+}$	A	−467.203725(19404)	0.0		0.0	
$[Rh(NH_3)_5{\cdots}OH_2^{3+}]^\ddagger$	A	−467.155381(175)	126.9		1.21	
$Rh(NH_3)_5{\cdot}OH_2^{3+}$	A	−467.160298(19404)	114.0		1.68	
$Rh(NH_2CH_3)_5OH_2{\cdot}OH_2^{3+}$	B	−738.900233(3)	0.0		0.0	
[*cis*-$Rh(NH_2CH_3)_5{\cdots}(OH_2)_2^{3+}]^\ddagger$	B	−738.865446(3)	91.3	113 ± 2/101[d]	0.15	1.2 ± 1.1[d]
$Rh(NH_2CH_3)_5OH_2^{3+}$	B	−662.665505(20)	0.0		0.0	
$[Rh(NH_2CH_3)_5{\cdots}OH_2^{3+}]^\ddagger$	B	−662.630768(20)	91.2	113 ± 2/101[d]	1.24	1.2 ± 1.1[d]
$Rh(NH_2CH_3)_5{\cdot}OH_2^{3+}$	B	−662.632548(20)	86.5		1.71	

[a] In parentheses: number of configuration state functions for the CAS−SCF wave function. [b] Reference 12. [c] Electronic triplet ($^3A''$) state. [d] Reference 15.

there are two nonbonding (d_α), two moderately antibonding (d_β), and one strongly antibonding (d_γ) d orbitals.[2,6] In complexes of second-row transition metals, for example, those of ruthenium(III) and rhodium(III), the corresponding qualitative orbital diagram is similar, and the small differences with respect to first-row transition metals will be discussed in this article. In these heptacoordinated species, the nearly degenerate nonbonding d_α levels are filled with four electrons, and the lower of the two d_β levels is populated with one or two electrons for ruthenium(III) or rhodium(III), respectively. Because of the fewer electron in the antibonding d_β level, a heptacoordinated species with a ruthenium(III) center is expected to be more stable and to have shorter metal−ligand bond lengths than the corresponding rhodium(III) species. Because in both (pseudo-octahedral) $M(NH_3)_5OH_2^{3+}$ (M = Ru or Rh) reactants, which both undergo water exchange via an interchange mechanism, only nonbonding d_π levels are occupied, one would expect a more negative *intrinsic* component of the activation volume ($\Delta V_{int}^\ddagger$) for reaction 2 compared with that for reaction 3. Although the pentaammine complexes of cobalt(III) and rhodium(III) are valence isoelectronic, the volumes of activation for their water-exchange reactions are sufficiently different (namely, 1.2 and −4.1 cm^3/mol,[12,13] respectively) that the two reactions might proceed via disparate mechanisms. Whereas for pentaammine complexes of cobalt(III) the I_d mechanism operates,[8,9,13,14] the moderately negative volume of activation for the corresponding complexes of rhodium(III) would suggest the I_a mechanism.

Another interesting experimental observation is that, by replacing the ammonia ligands of $Rh(NH_3)_5OH_2^{3+}$ with the bulky methylamine ones, the volume of activation for the water-exchange increases by 5.3 cm^3/mol, such that the volume of activation for reaction 4 is slightly positive (namely, 1.2 cm^3/mol).[15]

$$Rh(NH_2CH_3)_5OH_2^{3+} + \mathbf{H_2O} \rightarrow Rh(NH_2CH_3)_5\mathbf{OH_2}^{3+} + H_2O \quad (4)$$

It is interesting to note that the activation volume for the water-exchange on $Co(NH_3)_5OH_2^{3+}$ is exactly the same as that on $Rh(NH_2CH_3)_5OH_2^{3+}$.[13,15] To get a deeper understanding into the water-exchange mechanism of pentaamine complexes of rhodium(III), reactions 3 and 4 were investigated with quantum chemical calculations.

Results

Computational Method and Model. The present calculations, which take into account hydration and electron correlation, were performed as described for $Ru(NH_3)_5OH_2^{3+}$.[7] The geometries were optimized on the basis of the self-consistent reaction field model (SCRF),[16−18] and the energies were computed using the polarizable continuum model (PCM)[19−21] at the complete active space self-consistent field (CAS−SCF) level. Electron correlation was treated with the ‘multiconfigurational self-consistent field second-order quasidegenerate perturbation’ (MCQDPT2) method[22,23] as described.[7] Neglected is the dispersion (correlation between the complex and the solvent). The zero point energy (ZPE) was not included because with this model, in which the second coordination sphere is not treated quantum chemically, it is meaningless, and so are also the calculated activation entropies ($\Delta S_{298}^\ddagger$).[6,9] The most favorable exchange pathway has the lowest $\Delta G_{298}^\ddagger$. The quantum chemically computed activation energies ($\Delta E^\ddagger$) correspond approximately to $\Delta H^\ddagger$ at 0 K with the contribution of the ZPEs neglected. Because the present model does not allow the computation of $\Delta S_{298}^\ddagger$, $\Delta G_{298}^\ddagger$ cannot be calculated, and the most advantageous exchange pathway can only be rationalized or predicted if the corresponding $\Delta E^\ddagger$ values differ substantially.

The associative (A), interchange (I_a, I, or I_d), and dissociative (D) mechanisms were investigated on the basis of eqs 5, 6, and 7, respectively, where A represents an amine ligand, either NH_3 or NH_2CH_3.

$$Rh\,A_5\,OH_2{\cdot}OH_2^{3+} \rightarrow [Rh\,A_5\,OH_2{\cdots}OH_2^{3+}]^\ddagger \quad (5)$$

$$Rh\,A_5\,OH_2{\cdot}OH_2^{3+} \rightarrow [Rh\,A_5{\cdots}(OH_2)_2^{3+}]^\ddagger \quad (6)$$

$$Rh\,A_5\,OH_2^{3+} \rightarrow [Rh\,A_5{\cdots}OH_2^{3+}]^\ddagger \quad (7)$$

The geometries of all relevant stationary points on the potential energy surface, reactants/products, transition states, and intermediates, if there are any, were optimized without constraints and the activation energies were calculated.

The atomic coordinates of all computed structures are given in Tables S1−S12 (Supporting Information). The total energies, activation energies and the change of the sum of the rhodium-ligand (Rh-L) bond lengths, $\Delta\sum d(\text{Rh-L})$, which occur during the activation processes (5−7) are reported in Table 1. All Rh-L bond lengths and their sums are given in Table 2.

Water-Exchange on $Rh(NH_3)_5OH_2^{3+}$ via Interchange Mechanisms. These computations were performed on the basis of eq 6. The attack of a water molecule adjacent to the aqua ligand leads to the transition state [*cis*-$Rh(NH_3)_5{\cdots}(OH_2)_2^{3+}]^\ddagger$ (Figure 1) with C_1 symmetry. It is similar to that of the corresponding ruthenium(III) species.[7] Selected bond lengths are reported in Table 2: the two Rh⋯O bond lengths of 3.13 Å are, on the average, longer by 0.44 Å than those in the

TABLE 2: Rhodium(III)−Ligand Bond Lengths and Change of Their Sum During the Activation[a]

Species	d(Rh-N)	d(Rh-O)	∑d(Rh-N)	∑d(Rh-L)	Δ∑d(Rh-N)	Δ∑d(Rh-L)
(i) Basis set A:						
$Rh(NH_3)_5OH_2{\cdot}OH_2^{3+}$	2.153, 2.142, 2.117, 2.143, 2.141	2.121, 4.033	10.696	16.850	0.0	0.0
$Rh(NH_3)_5OH_2{\cdot}OH_2^{3+}$ (^3A state)	2.163, 2.164, 2.430, 2.164, 2.152	2.367, 4.116	11.073	17.556	0.377	0.706
[*cis*-$Rh(NH_3)_5{\cdots}(OH_2)_2^{3+}]^{\ddagger}$	2.131, 2.124, 2.062, 2.145, 2.129	3.173, 3.096	10.591	16.860	−0.105	0.010
$[Rh(NH_3)_5{\cdots}(OH_2)_2^{3+}]^{\ddagger}$ [b]	2.152, 2.132, 2.117, 2.233[c]	3.280[c]	10.867	17.427	0.171	0.577
$Rh(NH_3)_5OH_2^{3+}$	2.144, 2.152, 2.109, 2.151, 2.143	2.159	10.699	12.858	0.0	0.0
$[Rh(NH_3)_5{\cdots}OH_2^{3+}]^{\ddagger}$	2.124,[c] 2.056, 2.149[c]	3.461	10.602	14.063	−0.097	1.205
$Rh(NH_3)_5{\cdot}OH_2^{3+}$	2.131,[c] 2.058, 2.148[c]	3.922	10.616	14.538	−0.083	1.680
$Rh(NH_2CH_3)_5OH_2{\cdot}OH_2^{3+}$	2.159, 2.151, 2.118, 2.170, 2.159	2.136, 4.058	10.757	16.951	0.0	0.0
[*cis*-$Rh(NH_2CH_3)_5{\cdots}(OH_2)_2^{3+}]^{\ddagger}$	2.136, 2.142, 2.064, 2.146, 2.165	3.164, 3.275	10.653	17.092	−0.104	0.141
$Rh(NH_2CH_3)_5OH_2^{3+}$	2.163, 2.161, 2.110, 2.159, 2.160	2.177	10.753	12.930	0.0	0.0
$[Rh(NH_2CH_3)_5{\cdots}OH_2^{3+}]^{\ddagger}$	2.143, 2.133, 2.058, 2.148, 2.173	3.513	10.655	14.168	−0.098	1.238
$Rh(NH_2CH_3)_5{\cdot}OH_2^{3+}$	2.143, 2.145, 2.058, 2.143, 2.172	3.980	10.661	14.641	−0.092	1.711
(ii) Basis set B:						
$Rh(NH_2CH_3)_5OH_2{\cdot}OH_2^{3+}$	2.157, 2.149, 2.115, 2.167, 2.157	2.137, 4.059	10.745	16.941	0.0	0.0
[*cis*-$Rh(NH_2CH_3)_5{\cdots}(OH_2)_2^{3+}]^{\ddagger}$	2.134, 2.140, 2.062, 2.143, 2.163	3.165, 3.279	10.642	17.086	−0.103	0.145
$Rh(NH_2CH_3)_5OH_2^{3+}$	2.160, 2.158, 2.107, 2.156, 2.158	2.178	10.739	12.917	0.0	0.0
$[Rh(NH_2CH_3)_5{\cdots}OH_2^{3+}]^{\ddagger}$	2.140, 2.131, 2.056, 2.145, 2.171	3.516	10.643	14.159	−0.096	1.242
$Rh(NH_2CH_3)_5{\cdot}OH_2^{3+}$	2.141, 2.142, 2.056, 2.140, 2.170	3.981	10.649	14.630	−0.090	1.713

[a] Units: angstroms. [b] Attack opposite to the leaving group. [c] Two symmetry equivalent bonds.

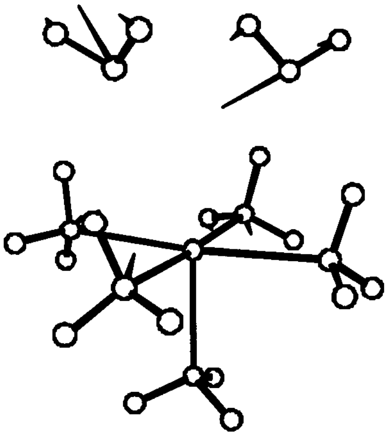

Figure 1. Perspective view and imaginary mode of the transition state [*cis*-$Rh(NH_3)_5{\cdots}(OH_2)_2^{3+}]^{\ddagger}$ (I mechanism; attack adjacent to the leaving water ligand).

corresponding ruthenium(III) species.[7] The reactant and product were obtained by the computation of the intrinsic reaction coordinate along which no intermediate was found. Despite the absence of any symmetry in the transition state, which leads to two disparate intrinsic reaction coordinates, the thus obtained reactant and product are identical and very similar to the corresponding ruthenium(III) compound.[7] The change of the sum of all Rh-L bond lengths, Δ∑d(Rh-L), along the activation process (eq 6) is approximately zero (+0.01 Å, Table 1). This result suggests the I mechanism for this pathway because the intrinsic component of the activation volume is expected to be approximately zero. The calculated activation energy is in perfect agreement with experiment (Table 1), although all specific interactions between the first and second coordination spheres are neglected.

Because, as will be shown later, water-exchange on $Rh(NH_3)_5$-OH_2^{3+} proceeds via the aforementioned I pathway, further calculations have been performed on the transition state [*cis*-$Rh(NH_3)_5{\cdots}(OH_2)_2^{3+}]^{\ddagger}$ to corroborate the adequacy of the computational model. In all the presently computed rhodium(III) complexes, there is some static electron correlation that was always taken into account in the calculations of the energy but not in those of the geometry. Thus, the structure of this transition state has also been optimized at the CAS−SCF level with various active spaces (Table 3). These calculations yielded longer Rh-N and Rh···O bonds. The larger the active space, the more closely the geometry approached that obtained at the Hartree−Fock level (Table 2). This result shows that the latter is adequate for the geometry optimizations.

Attempts to calculate a transition state for the attack of the entering water opposite the aqua ligand, which would give rise to inversion of the configuration, failed for the singlet electronic state but were successful for the triplet state. Also, this species, $[Rh(NH_3)_5{\cdots}(OH_2)_2^{3+}]^{\ddagger}$ (Figure 2), with C_s symmetry, is similar to the corresponding ruthenium(III) analogue.[7] Because in the triplet electronic state ($^3A''$) of this (heptacoordinated) transition state, two electrons are located in two moderately antibonding 4d orbitals (d_β),[2,6] two Rh-N bonds are longer by ~0.1 Å than the three others (Table 2). Compared with [*cis*-$Rh(NH_3)_5{\cdots}(OH_2)_2^{3+}]^{\ddagger}$, the Rh···O bonds are longer by 0.15 Å on the average. The attack opposite to the aqua ligand is very unlikely to occur because this reaction requires an activation energy (Table 1) that is higher by >100 kJ/mol compared with that for the adjacent attack (which leads to retention of the configuration). The change of the sum of the Rh-L bond lengths (Table 1), Δ∑d(Rh-L), is positive, and therefore, this value would suggest the I_d mechanism. In the following, it will be shown that in substitution reactions that involve spin changes, the attribution of the mechanism is not straightforward.

If spin changes arise from the promotion of one or more electrons from nonbonding into antibonding orbitals, the metal−ligand bonds (M-L), in which these antibonding electrons are located, are elongated whereas the others are not altered much. The spin change alone thus causes an increase of the sum of the M-L bonds, and this change gives rise to an increase in the intrinsic volume of the complex. This situation is illustrated by the example of the reactant $Rh(NH_3)_5OH_2{\cdot}OH_2^{3+}$, in which the Rh-O bond and the corresponding trans Rh-N bond are both elongated by 0.25 and 0.31 Å in the lowest, thermally relaxed, triplet electronic state (Table 2). This elongation arises from the promotion of a nonbonding $4d_\pi$ electron into the antibonding d_σ*(O-Rh-N) orbital. This spin change causes an increase of the Δ∑d(Rh-L) parameter by 0.71 Å. It should be noted that reactions that involve such spin changes are likely to have positive intrinsic volumes of activation, just because of the increase of the M-L bonds due to the spin change. If the exchange process starting from the reactant in the triplet state is considered, a negative Δ∑d(Rh-L) value of −0.13 Å would be obtained, which would suggest the I_a mechanism for this

TABLE 3: Rhodium(III)−Ligand Bond Lengths of the Transition State [*cis*-$Rh(NH_3)_5\cdots(OH_2)_2^{3+}]^{\ddagger}$ Optimized at the CAS−SCF Level[a]

Number of active orbitals	Number of electrons	Number of CSFs[b]	d(Rh-N)	d(Rh-O)
—	—	1[c]	2.131, 2.124, 2.062, 2.145, 2.129	3.173, 3.096
2	2	3	2.135, 2.127, 2.077, 2.152, 2.133	3.280, 3.180
4	4	20	2.154, 2.130, 2.079, 2.154, 2.139	3.294, 3.170
6	6	175	2.154, 2.129, 2.078, 2.153, 2.138	3.284, 3.162
8	8	1764	2.154, 2.129, 2.078, 2.151, 2.137	3.259, 3.142

[a] Units: angstroms. [b] CSFs: configuration state functions. [c] Hartree−Fock calculation; the same data as in Table 2.

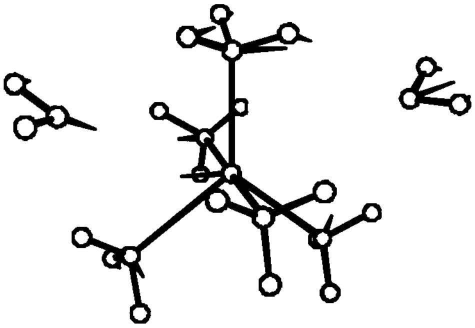

Figure 2. Perspective view and imaginary mode of the transition state $[Rh(NH_3)_5\cdots(OH_2)_2^{3+}]^{\ddagger}$ with C_s symmetry (I_d mechanism; attack opposite to the leaving water ligand).

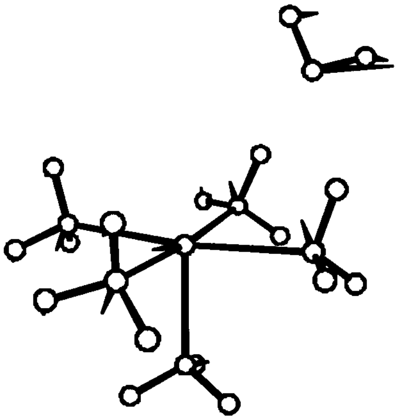

Figure 3. Perspective view and imaginary mode of the transition state $[Rh(NH_3)_5\cdots OH_2^{3+}]^{\ddagger}$ with C_S symmetry (D mechanism).

pathway. It is evident that in such cases, the attribution of the substitution mechanism on the basis of the intrinsic activation volume, $\Delta V_{int}^{\ddagger}$, is not straightforward, because $\Delta V_{int}^{\ddagger}$ has two components, one arising from the spin change and the other one from the substitution reaction itself.

Water-Exchange on $Rh(NH_3)_5OH_2^{3+}$ via the D Mechanism. The calculations for this pathway were performed on the basis of eq 7. The transition state, $[Rh(NH_3)_5\cdots OH_2^{3+}]^{\ddagger}$ (Figure 3), has C_s symmetry, and it is again similar to that of the analogous ruthenium(III) species.[7] The pentacoordinated intermediate, $Rh(NH_3)_5{\cdot}OH_2^{3+}$ (Figure 4), also with C_s symmetry, resembles the corresponding transition state (Figure 3), but the leaving water ligand is more distant from the rhodium(III) center (Table 2). The reactant/product has C_1 symmetry. The activation energy (Table 1) is moderately higher, by ~25 kJ/mol, than that for the most favorable interchange pathway. The Rh···O bond length is longer by 0.33 Å than those in [*cis*-$Rh(NH_3)_5\cdots(OH_2)_2^{3+}]^{\ddagger}$. This mechanism is unlikely to operate for reaction 3 because of its higher activation energy. Furthermore, it would give rise to a positive volume of activation that would be at variance with the negative experimental[12] value. In strained or constrained complexes, however, the D mechanism might be preferred over the interchange one, as will be shown in the next section.

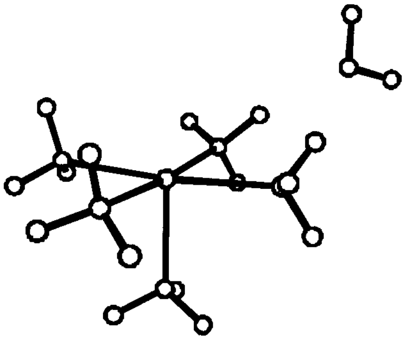

Figure 4. Perspective view of the pentacoordinated intermediate $Rh(NH_3)_5{\cdot}OH_2^{3+}$ with C_s symmetry (D mechanism).

In earlier work,[2] arguments have been presented suggesting that for a low-spin d^6 electron configuration, the rearrangement of a square pyramidal pentacoordinated intermediate into a trigonal bipyramid is unfavorable. Thus, this pathway would also proceed with retention of the configuration.

Basis Sets Used in the Computation of the Water-Exchange on $Rh(NH_2CH_3)_5OH_2^{3+}$. The calculation of electron correlation using the MCQDPT2 method[22,23] for the species involved in reaction 4 is demanding and was not feasible with the available hardware, when basis set A, in which there are polarization functions on all C, N, and O atoms, was used. Because the methyl groups of methylamine are not coordinated to the rhodium(III) center, the polarization functions on the C atoms were omitted in a smaller basis set B. It can be seen that there is no loss of accuracy in the geometries when basis set B was used; it gave rise to slightly shorter (by 0.003 Å) Rh-N and Rh-O bond lengths (Table 2). All geometry optimizations were performed using both basis sets, but the total and activation energies were computed with basis set B only (Table 1).

Water-Exchange on $Rh(NH_2CH_3)_5OH_2^{3+}$ via Interchange Mechanisms. Because for $Rh(NH_3)_5OH_2^{3+}$ the attack opposite to the leaving water ligand requires a very high activation energy (228 kJ/mol, Table 1), only the pathway for the adjacent attack was investigated. The transition state [*cis*-$Rh(NH_2CH_3)_5\cdots(OH_2)_2^{3+}]^{\ddagger}$ (Figure 5) resembles the ammonia analogue (Figure 1) very much. It is interesting to note that the CH_3 groups are located in the 'lower half' of the octahedron, which is represented by the RhN_5 chromophore. The Rh-N bonds in [*cis*-$Rh(NH_2CH_3)_5\cdots(OH_2)_2^{3+}]^{\ddagger}$ are longer by ~0.01 Å in the average than those of the NH_3 analogue, but the corresponding Rh···O bonds are considerably longer, by ~0.09 Å on the average (Table 2).

The reactant $Rh(NH_2CH_3)_5OH_2{\cdot}OH_2^{3+}$ (Figure 6) was obtained by the computation of the intrinsic reaction coordinate. Again, the Rh-N, Rh-O, and Rh···O bonds are longer by ~0.01, 0.015, and 0.025 Å, respectively, than in the corresponding

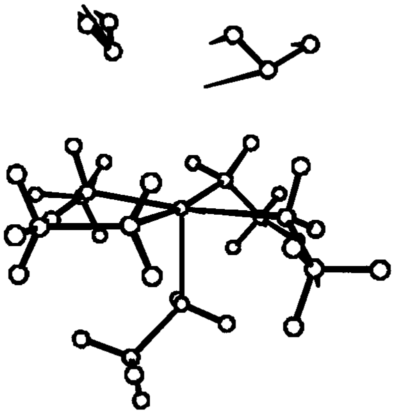

Figure 5. Perspective view and imaginary mode of the transition state [*cis*-Rh$(NH_2CH_3)_5\cdots(OH_2)_2^{3+}]^{\ddagger}$ (I_d mechanism; attack adjacent to the leaving water ligand).

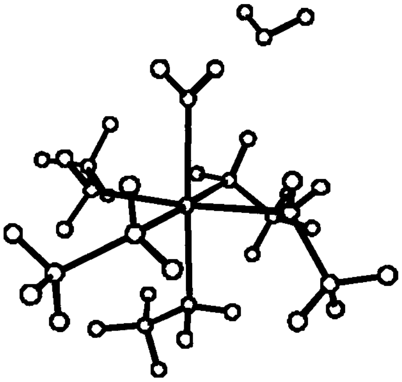

Figure 6. Perspective view of the reactant/product Rh$(NH_2CH_3)_5OH_2\cdot OH_2^{3+}$ (I_d mechanism; attack adjacent to the leaving water ligand).

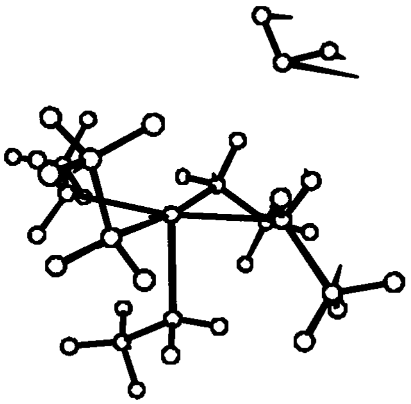

Figure 7. Perspective view and imaginary mode of the transition state [Rh$(NH_2CH_3)_5\cdots OH_2^{3+}]^{\ddagger}$ (D mechanism).

ammonia complex. Because of the longer Rh$\cdots$O bonds in [*cis*-Rh$(NH_2CH_3)_5\cdots(OH_2)_2^{3+}]^{\ddagger}$, the $\Delta\Sigma$d(Rh-L) value is larger for reaction 4 than 3 (Tables 1 and 2). On the basis of this positive $\Delta\Sigma$d(Rh-L) parameter, the intrinsic volume of activation would be positive, and therefore, this interchange pathway would be of the I_d type.

The calculated activation energy is lower than $\Delta H_{298}^{\ddagger}$ by 22 kJ/mol (Table 1). This error is in contrast to the accurate value computed for the corresponding NH_3 complex.

Water-Exchange on Rh$(NH_2CH_3)_5OH_2^{3+}$ via the D Mechanism. Reactant/product, transition state (Figure 7), and pentacoordinated intermediate (Figure 8) all have C_1 symmetry, and the RhN_5O skeleton is the same as that of the corresponding species with NH_3 ligands. This result can be seen by comparing the two transition states for the D mechanism (Figures 3 and 7). It should be noted that there are small, but noticeable differences between the analogous ammonia and methylamine complexes: in the latter, the average Rh-N bonds are longer by 0.011 Å, and the Rh-O bonds are longer by 0.019 and 0.052 Å in the reactant and transition state, respectively (Table 2). Interestingly, for the D mechanism, the $\Delta\Sigma$d(Rh-N) and $\Delta\Sigma$d(Rh-L) parameters are the same for the ammonia and methylamine complexes.

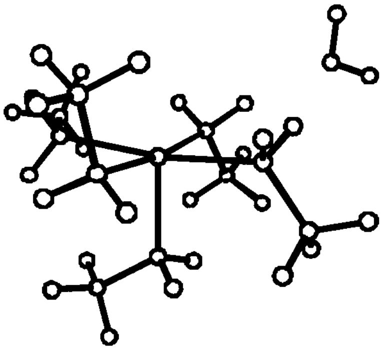

Figure 8. Perspective view of the pentacoordinated intermediate Rh$(NH_2CH_3)_5\cdot OH_2^{3+}$ (D mechanism).

The calculated activation energy (Table 1) is equal to that for the interchange pathway and also too low by 22 kJ/mol. In this case, the computed activation energies do not allow the distinction of the I_d from the D mechanism.

Discussion

Activation Energies. For the water-exchange on Rh$(NH_3)_5OH_2^{3+}$ via the I mechanism, the calculated activation energy agrees within a few kilojoules/mole with $\Delta H_{298}^{\ddagger}$ (Table 1). This accuracy could not be expected on the basis of this model, which neglects all specific interactions between the first and second coordination spheres.[6] Interestingly, the same accuracy was obtained for the activation energy for the water-exchange on Ru$(NH_3)_5OH_2^{3+}$, and this reaction also follows an interchange mechanism (I_a) with retention of the configuration.[7] The other two investigated pathways for reaction 3, the interchange mechanism with stereomobility and the D mechanism, both require higher activation energies and are therefore unlikely to operate.

For the water-exchange on Rh$(NH_2CH_3)_5OH_2^{3+}$, equal activation energies were computed for the I_d and the D mechanisms. They are both too low by 22 kJ/mol compared with $\Delta H_{298}^{\ddagger}$.[12] This error is considerably larger than that of reactions 2 and 3, which both involve complexes with NH_3 ligands. Therefore, this relatively large error may be due to the CH_3NH_2 ligands or the limitations[6] of the model.

The error just mentioned is unlikely to arise from the omission of the polarization functions on the C atoms because the latter are quite remote from the rhodium(III) center and the C−H and C−N bonds do not interfere in the present substitution reactions. Most likely, the following three reasons give rise to this error: (i) The reactant might not be in its most stable conformation because it has been obtained by computations of the intrinsic reaction coordinate. The presently obtained local minimum might not be the global one, which is hard to find because of the large number of possible conformers; (ii) The PCM might not be appropriate for such compounds in which the water molecules in the second sphere are ‘perturbed’ by the hydrophobic methyl groups or, in other words, the water layer in the second coordination sphere contains five hydrophobic methyl

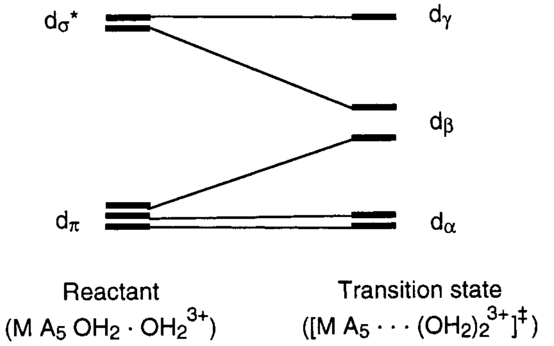

Figure 9. Qualitative orbital diagram of reactants/products $MA_5OH_2^{3+}$ and transition states $[MA_5\cdots(OH_2)_2^{3+}]^{\ddagger}$.

groups. It could be that in such compounds, the H_2O molecules of the second coordination sphere have to be treated quantum chemically and that the PCM should be applied from the third coordination sphere on; (iii) There is no reason the model represented by eqs 5−7 must reproduce the activation energies accurately, but it most likely does so for the hexaaqua ions[6] and for the aqua pentammine complexes of Ru^{III} and Rh^{III} because the changes in the first coordination sphere are calculated explicitly. However, for interchange mechanisms, the energy involved in all changes of H-bonding between the first and the second coordination spheres is represented merely by the breaking of two H-bonds in the water adduct of the reactant. The correct reproduction of this energy term by the present model is of course fortuitous. The reorganizational energy of the bulk solvent is taken into account by the PCM.[19−21]

If the second coordination sphere is treated quantum chemically, the conformation of the CH_3 groups might be different from those obtained by the inclusion of water as a dielectric continuum. Therefore, correct activation energies might only be available when both items (i) and (ii) are considered. Today, such calculations are hardly feasible. The important results are that reaction 4 proceeds via a dissociative pathway with retention of the configuration, and that the I_d and D mechanisms have very similar activation energies but different $\Delta\Sigma$d(Rh-L) values. It should be noted that, therefore, the intrinsic activation volumes would be different. This point will be discussed in another section of this discussion.

Electronic Structure of the Transition States [*cis*-$MA_5\cdots(OH_2)_2^{3+}]^{\ddagger}$ (M = Ru and Rh). The electronic structure has already been discussed for the heptacoordinated intermediates and transition states formed in the water exchange of first-row transition metal hexaaqua ions.[2,6] The electronic structure of the transition states of the aqua pentaamine complexes of the second-row metal ions Ru^{III} and Rh^{III} is similar. The difference with respect to first-row transition metals is that the d_β levels are split more strongly in complexes of second-row metals. In the transition state $[Co(NH_3)_5\cdots(OH_2)_2^{3+}]^{\ddagger}$, with a triplet electronic state, the two d_β levels that are each populated by one electron are split by 0.1 eV;[24] for the corresponding valence isoelectronic Rh^{III} complex, this splitting is 0.6 eV. This larger energy difference arises from the larger crystal field parameter of second-row elements. Thus, in transition states for interchange mechanisms, the five 4d levels are split into two nearly degenerate nonbonding d_α levels, two moderately antibonding d_β level, and a strongly antibonding d_γ level (Figure 9).

The two $Rh^{III}\cdots O$ bonds involve two oxygen-centered, bonding $\sigma(Rh^{III}\cdots O)$ orbitals (Figure 10) and two Rh^{III}-centered, antibonding $\sigma^*(Rh^{III}\cdots O)$ orbitals (Figure 11), which are the d_β levels (Figure 9). In the transition states [*cis*-$Rh(NH_3)_5\cdots(OH_2)_2^{3+}]^{\ddagger}$ and [*cis*-$Rh(NH_2CH_3)_5\cdots(OH_2)_2^{3+}]^{\ddagger}$, the lower d_β level (Figure 11a) is populated by a pair of electrons, whereas the other one (Figure 11b) is empty. In the corresponding transition state of Ru^{III}, the lower d_β level is occupied by a single d_β electron only. Because there is one fewer electron in the (antibonding) d_β levels, the $Ru^{III}\cdots O$ bonds are stronger and shorter than those of Rh^{III}, and this is illustrated by their respective average bond lengths of 2.69[7] and 3.13 Å.[25] This difference might change slightly on the addition of a quantum chemically treated second coordination sphere, but the $Ru^{III}\cdots O$ bonds will remain much shorter than the $Rh^{III}\cdots O$ bonds.[26] In general, the M···O bond lengths depend on the number of electrons in the d_β levels. The $\Delta\Sigma$d(M-L) parameters for Rh^{III} and Ru^{III} follow the same trend; they have the respective values of 0.01 and −0.82 Å. Thus, the *intrinsic component* of the activation volume, $\Delta V_{int}^{\ddagger}$, is expected to be smaller (more negative) for Ru^{III} than for Rh^{III}, although the experimental[11,12] (total) activation volumes are equal for the water-exchange on these two aqua pentaammine complexes. This item will be discussed further in the next section.

In the transition state, in which the entering water would attack opposite to the leaving ligand, both d_β levels would each be occupied by a single electron.

Mechanism of the Water-Exchange Reactions. *(i)* $Rh(NH_3)_5OH_2^{3+}$. For this reactant, the most favorable pathway is the interchange process with retention of the configuration. On the basis of the $\Delta\Sigma$d(Rh-L) parameter (Table 1), which is approximately zero, an *intrinsic component* of the activation volume, $\Delta V_{int}^{\ddagger}$, of zero is expected. Because the experimental $\Delta V_{298}^{\ddagger}$ value is −4.1 cm^3/mol,[12] the calculations suggest that the *electrostrictive component* of the activation volume, $\Delta V_{el}^{\ddagger}$, is approximately −4 cm^3/mol, although a neutral ligand is exchanged. It has been shown in the previous section and elsewhere[7] that $\Delta V_{int}^{\ddagger}$ for the water-exchange of the corresponding Ru^{III} complex is negative. Because $\Delta V_{298}^{\ddagger}$ is equal for both metal ions, $\Delta V_{el}^{\ddagger}$ should be less negative for Ru^{III}, such that the two $\Delta V_{298}^{\ddagger}$ values, which are equal to the sum of $\Delta V_{int}^{\ddagger}$ and $\Delta V_{el}^{\ddagger}$, can be equal for Ru^{III} and Rh^{III}. *That $\Delta V_{int}^{\ddagger}$ is more negative for Ru^{III} than for Rh^{III} is a safe statement because, in the transition state [cis-$Ru(NH_3)_5\cdots(OH_2)_2^{3+}]^{\ddagger}$, there is one fewer electron in the lower antibonding d_β orbital (Figures 9 and 11a) than in the corresponding d_β level of [cis-$Rh(NH_3)_5\cdots(OH_2)_2^{3+}]^{\ddagger}$.* This result indicates that even for the similar mechanisms of reactions 2 and 3, which involve disparate structural changes in the activation process, $\Delta V_{el}^{\ddagger}$ is not equal. This inequality is probably due to the disparate dipole moments, partial charges, and sizes and shapes of the two transition states. Indeed, the $\Delta V_{el}^{\ddagger}$ term is known[16,27] to depend on these parameters.

On the basis of the $\Delta\Sigma$d(Rh-L) parameter, which is approximately zero (Table 1), the I mechanism would be attributed to reaction 3. For the water-exchange on $Ru(NH_3)_5OH_2^{3+}$ (reaction 2), this parameter is much more negative and, consequently, this reaction proceeds via the I_a mechanism.[7] The average $Rh^{III}\cdots O$ bond length of 3.13 Å in the transition state [*cis*-$Rh(NH_3)_5\cdots(OH_2)_2^{3+}]^{\ddagger}$ supplies further evidence for the I mechanism because this value lies between that calculated for reaction 3 via the D mechanism (3.46 Å) and that calculated for reaction 2 via the I_a mechanism (2.67 Å).

(ii) $Rh(NH_2CH_3)_5OH_2^{3+}$. As already mentioned, the calculated activation energies for the I_d and D pathways are equal (Table 1) and too low by 22 kJ/mol. Possible reasons for this error have been discussed in the corresponding *Results Section*. The experimental activation volume for the water-exchange on this aqua pentaamine rhodium(III) complex, reaction 4, is 1.2 cm^3/

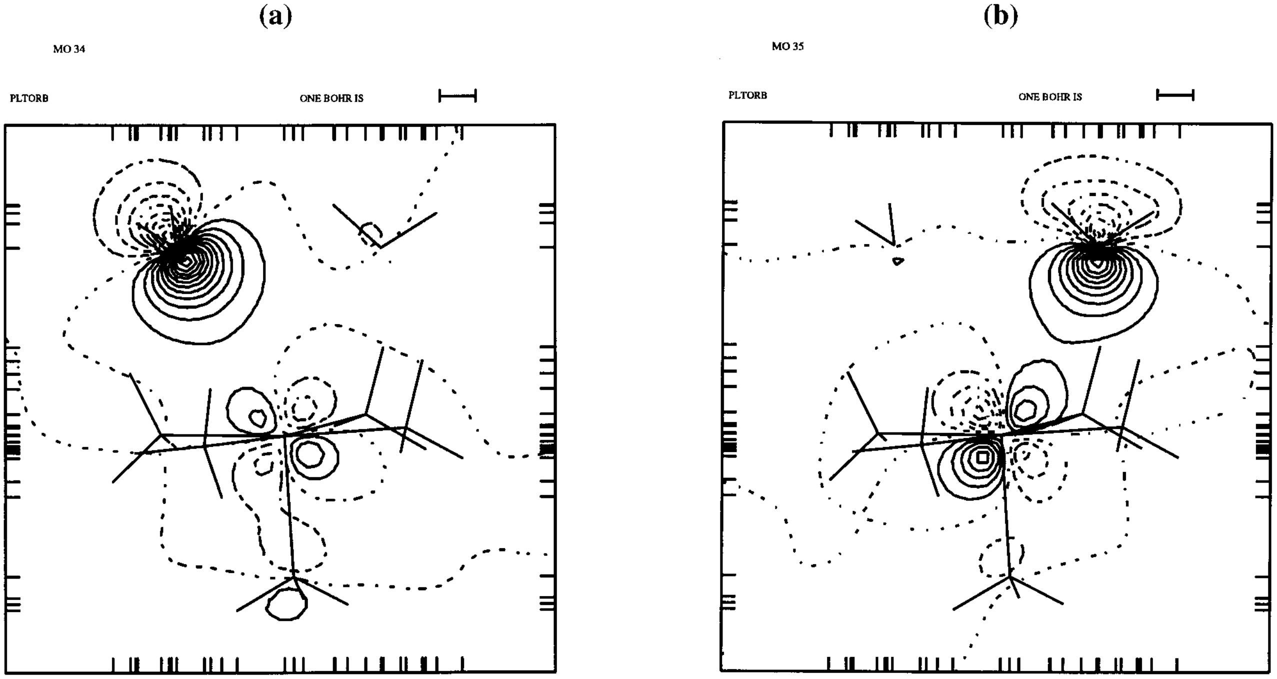

Figure 10. Contour plots depicting the two $\sigma(Rh^{III}\cdots O)$ orbitals of $[cis\text{-}Rh(NH_3)_5\cdots(OH_2)_2{}^{3+}]^{\ddagger}$: (a) MO 34; (b) MO 35.

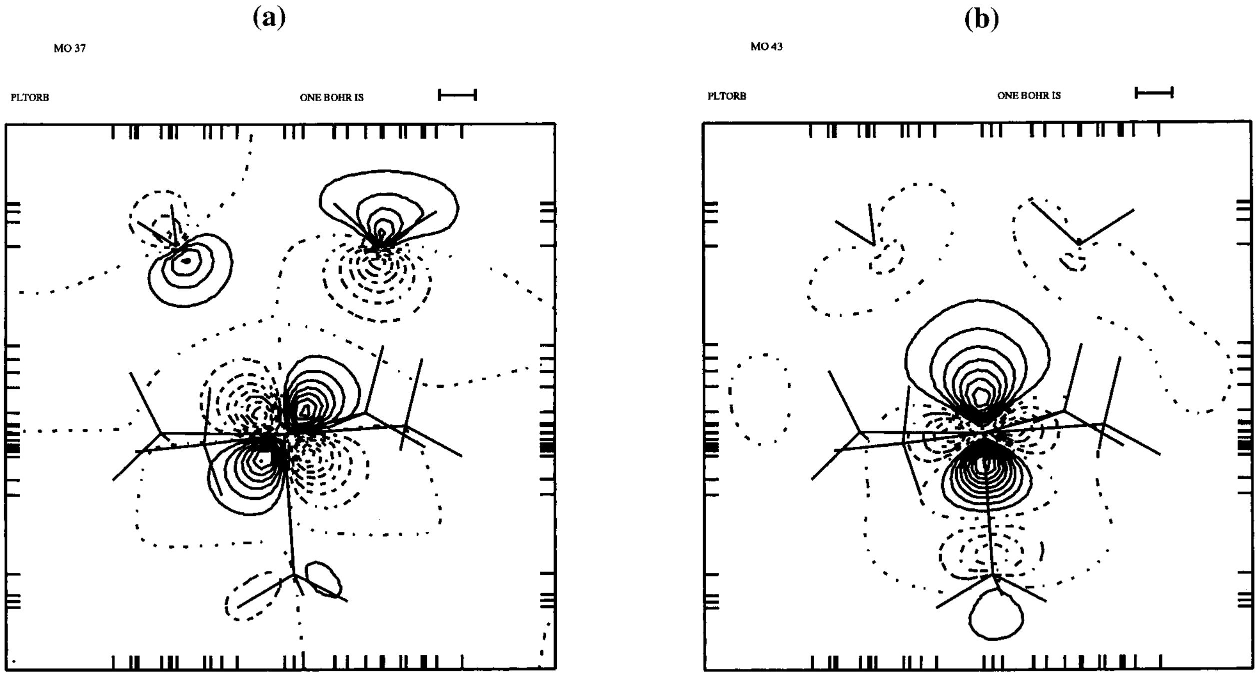

Figure 11. Contour plots depicting the two moderately antibonding $\sigma^*(Rh^{III}\cdots O)$ orbitals of $[cis\text{-}Rh(NH_3)_5\cdots(OH_2)_2{}^{3+}]^{\ddagger}$: (a) MO 37; (b) MO 43.

mol.[15] This value is larger by 5.3 cm^3/mol than that of the corresponding complex with ammonia ligands. This increase of $\Delta V_{298}^{\ddagger}$ on replacement of NH_3 by NH_2CH_3 is also reproduced by the corresponding increase of $\Delta\sum d(Rh\text{-}L)$. Because this parameter is not related quantitatively to $\Delta V_{298}^{\ddagger}$, it cannot be used for the distinction of the I_d from the D mechanism, which is very subtle anyway. Possibly, calculations in which at least the second coordination sphere is treated quantum chemically could lead to more precise activation energies, on the basis of which these two types of **d** activations could be distinguished. Also, perhaps, $\Delta V_{int}^{\ddagger}$ or $\Delta V_{el}^{\ddagger}$ could be computed at least approximately on the basis of this improved model. At the present time, such calculations are hardly feasible and therefore, from this study, it can only be concluded that the water-exchange on $Rh(NH_2CH_3)_5OH_2{}^{3+}$ (reaction 4) proceeds via a **d** activation, whereas both, the I_d or the D mechanism, could operate. In contrast to the calculations on $Ru(NH_3)_5OH_2{}^{3+}$ and $Rh(NH_3)_5OH_2{}^{3+}$, which yielded quantitative results, those on $Rh(NH_2CH_3)_5OH_2{}^{3+}$ are less accurate.

Summary

(i) The water-exchange reactions on $Ru(NH_3)_5OH_2{}^{3+}$, $Rh(NH_3)_5OH_2{}^{3+}$, and $Rh(NH_2CH_3)_5OH_2{}^{3+}$ follow the respective I_a, I, and I_d (or D) mechanisms.

(ii) The more associative character of Ru^{III} (a low-spin d^5 system) with respect to Rh^{III} (a low-spin d^6 system) is due to the occupation of the moderately antibonding (d_β) orbitals in the transition state. The $Ru^{III}\cdots O$ bonds are shorter than the $Rh^{III}\cdots O$ ones, because in the transition state [*cis*-$Ru(NH_3)_5\cdots(OH_2)_2{}^{3+}]^{\ddagger}$ the lower of these (d_β) levels is populated by one electron, whereas in [*cis*-$Rh(NH_3)_5\cdots(OH_2)_2{}^{3+}]^{\ddagger}$, this same ($d_\beta$) level is populated by a pair of electrons. For these interchange mechanisms, the $M\cdots O$ bond lengths depend on the occupation of this level.

(iii) The water-exchange reactions on $Ru(NH_3)_5OH_2{}^{3+}$ and $Rh(NH_3)_5OH_2{}^{3+}$ exhibit equal activation volumes.[11,12] Because $\Delta\sum d(Ru\text{-}L)$[7] is more negative than $\Delta\sum d(Rh\text{-}L)$, $\Delta V_{int}{}^{\ddagger}$ of Ru^{III} is also expected to be more negative than $\Delta V_{int}{}^{\ddagger}$ of Rh^{III} and, therefore, $\Delta V_{el}{}^{\ddagger}$ is unequal for these two reactions and more negative for Rh^{III} than for Ru^{III}.

(iv) The replacement of the NH_3 ligands in $Rh(NH_3)_5OH_2{}^{3+}$ by the bulky NH_2CH_3 ones leads to longer $Rh^{III}\cdots O$ bonds in the transition state, and this gives rise to a **d** activation.

(v) The present model does not allow the distinction of the I_d from the D mechanism in the water-exchange on $Rh(NH_2CH_3)_5OH_2{}^{3+}$.

Computational Details

All calculations were performed on Cray T3D, HP 9000/C200, and HP 9000/735 computers using the GAMESS[28] programs.

The basis sets of Stevens, Basch, Krauss, and Jasien[29] were used for rhodium, where the 1s, 2s, 3s, 2p, 3p, and 3d shells are represented by relativistic effective core potentials, the 4s, 4p, 5s, and 5p shells have double-ζ quality, and the 4d shell has triple-ζ quality. For C, N, O, and H, 6-31G(d) basis sets[30,31] (basis set A) were used ($\alpha_{3d} = 0.80$, 1.00 and 1.20,[32] respectively). In basis set B, the polarization functions on the C atoms were omitted.

For the SCRF calculations,[16−18] the cavity radius was taken as half of the value of the largest interatomic distance plus the two corresponding van der Waals radii. Once the geometry had converged, the cavity radius was redetermined, and if it differed by >0.01 Å, from the previous value, the geometry optimization was repeated until the aforementioned criterion was fulfilled. All atomic coordinates are summarized in Tables S1−S12 (Supporting Information).

The active space for the CAS−SCF and multiconfigurational self-consistent field second-order quasidegenerate perturbation (MCQDPT2)[22,23] calculations was determined by the iterative natural orbital (INO) method.[33] Natural orbitals of a final CAS-CI calculation with occupations in the range of 0.015 to 1.985 were used for the active space of the CAS−SCF or MCQDPT2 steps. The energy computations based on the polarizable continuum model (PCM),[19−21] were performed at the CAS−SCF level, and the second-order perturbation energy of this wave function was calculated using the MCQDPT2 code (at the in vacuo level); the second-order contribution is equal to the second- minus the first-order energy [$E(MP2) - E(MCSCF)$]. The total PCM energy is equal to the PCM energy (CAS−SCF level) plus the second-order correction just mentioned.

The zero point energy was neglected for the reasons discussed in previous work.[1,2,6,9]

Acknowledgment. The ‘Service informatique central’ is acknowledged for computer time on the Cray T3D.

Supporting Information Available: A listing of the atomic coordinates of all reactants/products, transition states, and pentacoordinated intermediates (Tables S1−S12). This information is available free of charge via the Internet at http://pubs.acs.org.

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(26) The M−O bond lengths of trivalent transition metal hexaaqua ions diminish by 0.03−0.04 Å on the addition of 12 water molecules into the second coordination sphere.[24] Because the $Ru^{III}\cdots O$ and $Rh^{III}\cdots O$ bonds are weaker, these changes might be somewhat larger and disparate for Ru^{III} and Rh^{III}. The *difference* of the $Ru^{III}\cdots O$ and $Rh^{III}\cdots O$ bond lengths is, however, expected to alter only slightly.

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