Can Octahedral t_{2g}^6 Complexes Substitute Associatively? The Case of the Isoelectronic Ruthenium(II) and Rhodium(III) Hexaaquaions

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For the low-spin t_{2g}^6 $Ru(OH_2)_6^{2+}$ ($\Delta V^{\ddagger} = -0.4$ cm^3 mol^{-1}) and $Rh(OH_2)_6^{3+}$ ($\Delta V^{\ddagger} = -4.2$ cm^3 mol^{-1}) hexaaquaions, the respective I_d and I_a water exchange mechanisms had been assigned, mainly on the basis of activation volumes $\Delta V^{\ddagger}$ and entering ligands effects for water substitution. For Ru(II) the near-zero $\Delta V^{\ddagger}$ was supposed to be due to the compensation between a positive contribution (the loss of a water molecule) and a negative one (the contraction of the bonds of the five spectator ligands at the transition state). Recently, it has been suggested that Rh(III), because of its higher positive charge, could promote further spectator ligands bond contraction sufficient to change the sign of $\Delta V^{\ddagger}$ to a negative value. If true, this would be an example of limitation in the use of $\Delta V^{\ddagger}$ for a direct diagnosis of the mechanism. Quantum chemical calculations including hydration effects show that the activation energies for the water exchange on $Rh(OH_2)_6^{3+}$ via the I_a (114.8 kJ mol^{-1}) and the D pathways is 21.8 kJ mol^{-1} in favor of the former. In the case of $Ru(OH_2)_6^{2+}$ all attemps to compute a transition state for an interchange mechanism failed, but the calculated $\Delta E^{\ddagger}$ for the D mechanism (71.9 kJ mol^{-1}) is close to both experimental $\Delta G_{298}^{\ddagger}$ and $\Delta H_{298}^{\ddagger}$ values. The calculated $\Delta\sum d(M-O)$ values of -0.53 Å for rhodium(III) and $+1.25$ Å for ruthenium(II) agree with the experimented $\Delta V^{\ddagger}$ values and suggest I_a and D (or I_d) mechanisms, respectively. In the case of $Ru(OH_2)_6^{2+}$ the shortening of the bonds of the five spectator ligands to reach the transition states corresponds to a volume change of -1.7 cm^3 mol^{-1}. For $Rh(OH_2)_6^{3+}$ these spectator ligands' volume decrease is much smaller (maximum of -0.8 cm^3 mol^{-1}) and the bond lengths of the two exchanging ligands at the transition state are characteristic of an interchange pathway with a small "a" character. Because of the strong $Rh^{III}-O$ bonds, water exchange on $Rh(OH_2)_6^{3+}$ proceeds via the I_a pathway with retention of the configuration, whereas the same reaction of $Ru(OH_2)_6^{2+}$, which has considerably weaker $Ru^{II}-O$ bonds, follows the I_d or the D mechanism.

Introduction

Water exchange reactions on di- and trivalent transition metal aquaions have been the subject of extensive experimental studies and have been widely reviewed.[1,2] For 3d octahedral metal ions the water exchange mechanism progressively changes from I_a to I_d as the number of d electrons increases and the ionic radius decreases. This change is demonstrated most evidently by the change in sign of the activation volume $\Delta V^{\ddagger}$ and has been confirmed by Rotzinger,[3,4] who performed calculations at the Hartree−Fock or CAS-SCF level. The observed progressive mechanistic changeover cannot be explained in terms of cationic size only, the electronic configuration also playing an important role. For a σ-bonded octahedral complex, the t_{2g} orbitals are nonbonding, whereas the e_g^* orbitals are antibonding. The gradual filling of the t_{2g} orbitals, spread out between ligands, will electrostatically disfavor the approach of a seventh molecule toward a face or edge of the octahedron and therefore decreases the ease of bond-making. Similarly, an increased occupancy of the e_g^* orbitals, pointed to the ligands, will increase the bond-breaking tendency. The electronic effects can explain the changeover of mechanism.

According to these arguments, one would predict a dissociative activation mode for water exchange on the low-spin t_{2g}^6 hexaaquaions $Ru(OH_2)_6^{2+}$, $Rh(OH_2)_6^{3+}$, and $Ir(OH_2)_6^{3+}$. In the first study of the mechanism of substitution on $Ru(OH_2)_6^{2+}$, it was shown that the rate constants for the anation reactions by Cl^-, Br^-, and I^- were very similar, indicating identical steps to reach the transition state (i.e., dissociation of OH_2).[5] Later, this study was extended to a large variety of ligands possessing various charges and nucleophilicites, and it was clearly demonstrated that the rate of the monocomplex formation reactions was independent of the nature of the entering ligand. An I_d mechanism was therefore attributed for the substitution reactions on $Ru(OH_2)_6^{2+}$.[6] However, a variable pressure study of water exchange on this ion gave an activation volume close to zero ($\Delta V^{\ddagger} = -0.4$ cm^3 mol^{-1}) and was therefore interpreted as an interchange I mechanism without predominant "a" or "d" character.[7]

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The $Rh(OH_2)_6^{3+}$ aquaion is even more intriguing. By comparison of the rate constants of the Cl^- and Br^- anation with an ^{18}O labeling technique water exchange study (no incoming ligand dependence), a D mechanism was assigned.[8] A few years ago we obtained by high-pressure oxygen-17 NMR a negative volume of activation for $Rh(OH_2)_6^{3+}$ (-4.2 cm^3 mol^{-1})[9] and an even more negative one for $Ir(OH_2)_6^{3+}$ (-5.7 cm^3 mol^{-1})[10] and concluded in both cases that they were due to an associative interchange I_a mechanism. These last mechanistic assignments have recently been questioned. It had been suggested in the case of $Ru(OH_2)_6^{2+}$ that the near-zero $\Delta V^{\ddagger}$ value could be due to a bond contraction of the five spectator ligands in an I_d process to reach the transition state.[6,11] D. Richens has suggested that in the case of $Rh(OH_2)_6^{3+}$ the higher positive charge could promote further volume contraction in forming the pentaaqua transition state sufficient in this case to change the sign of $\Delta V^{\ddagger}$ to a negative value.[12] If true, this would be an example of limitation in the use of the overall activation volume $\Delta V^{\ddagger}$ for a direct diagnosis of the mechanism. It is the goal of this paper to resolve this discrepancy by using the theoretical approach developed successfully by Rotzinger during the recent years.

Computational Details

All calculations were performed on SGI workstations using the GAMESS[13] and the Gaussian 98[14] programs. The basis sets of Stevens et al.[15] were used for ruthenium and rhodium, where the 1s, 2s, 2p, 3s, 3p, and 3d shells are represented by relativistic effective core potentials; the 4s, 4p, 5s, and 5p shells exhibit double-ζ quality, and the 4d shell has triple-ζ quality. For oxygen and hydrogen, the 6-31G[16,17] basis set supplemented with a 3d polarization function ($\alpha_{3d}(O) = 1.20$)[18] was used.

All the calculations, in particular the location of the transition states, were performed with the method previously described by Rotzinger.[3,4] The ab initio calculations have been carried out at the restricted Hartree−Fock (SCF) level for the rhodium(III) species, previous calculations of Rotzinger[3,4] having shown that this level of theory leads to satisfactory results. This allowed us to characterize two water exchange mechanisms (dissociative and interchange) for this system. Since no seven-coordinated transition state could be found for the ruthenium(II) analogue, additional calculations performed at the MP2 level (to include dynamic correlation) and CAS-SCF (to take static correlation into account) have been carried out. Despite these efforts, no transition state for an interchange mechanism could be found.

The geometries of the reactants, transitions states, and pentacoordinated intermediate (for the D mechanism) were optimized at the Hartree−Fock level by taking into account solvation using the self-consistent reaction field model (SCRF)[19,20] implemented in the GAMESS program.[13,21] For the SCRF calculations, the cavity radius was taken as half 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 more than 0.01 Å from the previous value, the geometry optimization was repeated until the above criterion was fulfilled. Energies of these species were then computed on the basis of polarizable continuum models[22−26] (PCM and CPCM) using the Gaussian 98 program package.

Results

Model and Approximations. The water exchange of the isoelectronic hexaaquaions of rhodium(III) and ruthenium(II),

$$[M(OH_2)_6]^{n+} + 6H_2{*}O \rightleftharpoons [M({*}OH_2)_6]^{n+} + 6H_2O \quad (1)$$

was studied on the basis of the previously described[3,4] model. It involves the transition metal ion and six water molecules for the D mechanism,

$$[M(OH_2)_6]^{n+} \rightarrow \{[M(OH_2)_5\cdots OH_2]^{n+}\}^{\ddagger} \quad (2)$$

seven water molecules for the A mechanism,

$$[M(OH_2)_6{\cdot}OH_2]^{n+} \rightarrow \{[M(OH_2)_6\cdots OH_2]^{n+}\}^{\ddagger} \quad (3)$$

and the interchange mechanism,

$$[M(OH_2)_6{\cdot}OH_2]^{n+} \rightarrow \{[M(OH_2)_5\cdots(OH_2)_2]^{n+}\}^{\ddagger} \quad (4)$$

The geometries were optimized for all stationary points along the reaction paths, reactants/products, transition states, and intermediates (Figures 1 and 2). These calculations were performed for the hydrated ions as described in Table 1.[27−31]

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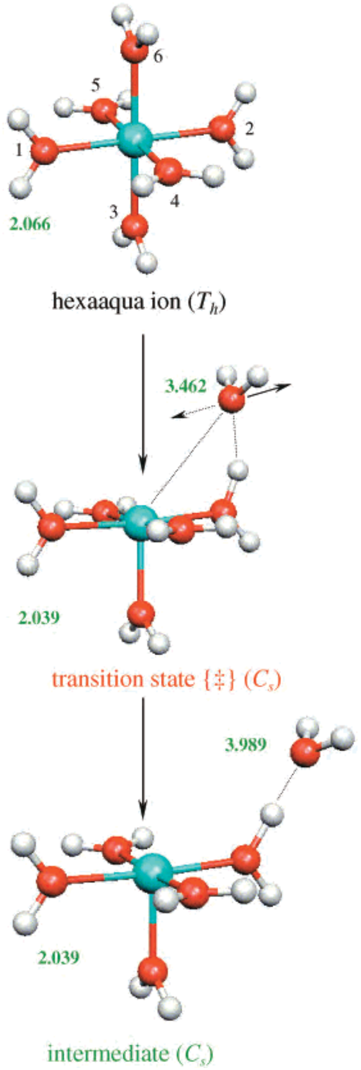

Figure 1. Transition state for the dissociative D mechanism. The M−O distances (average for the spectator ligands, left, and M−O(6), right) indicated are for rhodium(III). The imaginary mode for the transition state is indicated by arrows.

The changes of the sum of all M−O bond lengths,

$$\Delta\sum d(\text{M}-\text{O}) = \sum d(\text{M}-\text{O})_{\text{transition state}} - \sum d(\text{M}-\text{O})_{\text{reactant}} \quad (5)$$

during the activation is related to the intrinsic component of the volume activation ($\Delta V_{\text{int}}^{\ddagger}$). For the metal hexaaquaions, the sign of $\Delta\sum d(\text{M}-\text{O})$ was found to be the same as that of the volume of activation.[3,4,32]

The Hartree−Fock method is adequate for all rhodium(III) species as can be seen by the comparison of calculated and measured Rh−O bond lengths of $\text{Rh(OH}_2)_6^{3+}$ (Table 1). The error is the same as that for the hexaaquaions; the calculated Rh−O bond lengths are slightly too long, as already discussed.[3,4,33] The other approximations of this approach have also been discussed previously,[3,4,31] and these arguments are not repeated here.

In contrast, the calculated Ru−O bonds of $\text{Ru(OH}_2)_6^{2+}$ deviate considerably more from experimental results because in this case geometry optimizations at a level including static and dynamic electron correlation would be required. Such calculations could be performed using the CASPT2[34,35] or MCQDPT2[36,37] methods, which are computationally very demanding. Since, for the present purpose in the discussion of reaction mechanisms, accurate geometries are not really needed, the ruthenium(II) species were also computed at the Hartree−Fock level. This approximation is responsible for the too long Ru−O bonds of $\text{Ru(OH}_2)_6^{2+}$ (Table 1). These calculations are only qualitative and were performed for a comparison with the reactions of the isoelectronic rhodium(III) ions. Nevertheless, the calculated activation energy for the D mechanism does not deviate much from the experimental value.

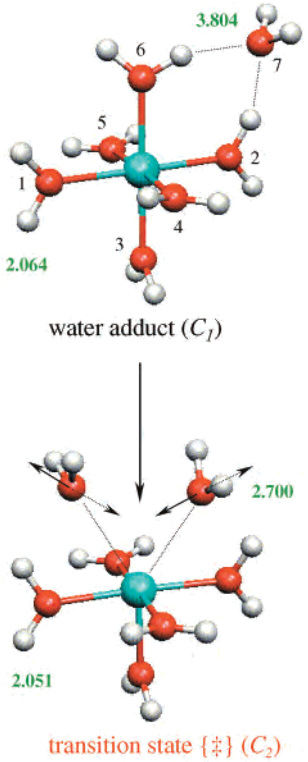

Figure 2. Transition state for the associative interchange I_a mechanism. The M−O distances (average for the spectator ligands, left, and M−O(7), right) indicated are for rhodium(III). The imaginary frequency mode for the transition state is indicated by arrows.

Water Exchange Mechanisms. For the rhodium(III) ion two transition states have been obtained, one for the dissociative (Figure 1) and one for the interchange (Figure 2) mechanisms, whereas for ruthenium(II), only that for the dissociative pathway could be calculated. All attempts of computations of a transition state for an interchange or associative mechanism on ruthenium(II) failed because the two $\text{Ru}^{\text{II}}\cdots\text{O}$ bonds are weaker than those of Rh^{III}. In the attempts of calculations of a transition state like $\{[\text{Rh(OH}_2)_5\cdots(\text{OH}_2)_2]^{2+}\}^{\ddagger}$, the two exchanging water molecules first moved away from the Ru^{II} center and then were attracted by the H atoms of the equatorial OH_2 ligands (those that are perpendicular to the equatorial plane). All structures converged toward the already described[3,4] dihydrate of the pentacoordinated intermediate, $\text{Ru(OH}_2)_5\cdot(\text{OH}_2)_2^{2+}$ (see, for example, Figure 9 of ref 3 or Figure 10 of ref 4). It is possible that a transition

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Table 1. Geometric and Thermodynamic Parameters Calculated (HF Level) for the Rh(III) and Ru(II) Species

		$\Delta E^‡$, kJ mol^{-1}			d(M−O), Å		
	symmetry	gas phase	PCM[b]	CPCM[b]	CPCM[c]	exptl	$\Delta\Sigma d$(M−O), Å
Rhodium(III), D Mechanism							
$[Rh(OH_2)_6]^{3+}$	T_h[a]				2.066; 2.066; 2.066; 2.066; 2.066; 2.066	2.016[d]	
$\{[Rh(OH_2)_5\cdots OH_2]^{3+}\}^‡$	C_s	136.6	136.6	131.3	2.077; 2.013; 2.006; 2.049; 2.049; 3.462		+1.260
$[Rh(OH_2)_5\cdot OH_2]^{3+}$	C_s	133.5	131.1	127.7	2.082; 2.008; 2.007; 2.049; 2.049; 3.989		+1.788
Rhodium(III), I_a Mechanism							
$[Rh(OH_2)_6\cdot(OH_2)]^{3+}$	C_1				2.081; 2.047; 2.071; 2.067; 2.067; 2.051; 3.804	2.016[d]	
$\{[Rh(OH_2)_5\cdots(OH_2)_2]^{3+}\}^‡$	C_2	134.6	114.8	112.9	2.052; 2.052; 2.026; 2.062; 2.062; 2.700; 2.700		−0.534
Ruthenium(II), D Mechanism							
$[Ru(OH_2)_6]^{2+}$	T_h[a]				2.209; 2.209; 2.209; 2.209; 2.209; 2.209	2.122[e]	
$\{[Ru(OH_2)_5\cdots OH_2]^{2+}\}^‡$	C_s	69.8	71.9	70.2	2.206; 2.163; 2.169; 2.188; 2.188; 3.589		+1.249
$[Ru(OH_2)_5\cdot OH_2]^{2+}$	C_s	68.1	61.5	60.1	2.208; 2.163; 2.168; 2.187; 2.187; 4.222		+1.881

[a] Optimized in D_{2h} symmetry. [b] Energies obtained using SCRF geometries, with hydration effects. [c] In the order of the oxygen numbering in Figures 1 and 2. [d] Average from X-ray structure of $Cs[Rh(OH_2)_6](SO_4)_2\cdot 6H_2O$.[27] EXAFS and large-angle X-ray scattering (LAXS) studies of $Rh(OH_2)_6^{3+}$ in solution give 2.03(2) Å.[28] [e] Average from X-ray structure of $[Ru(OH_2)_6](C_7H_7SO_3)_2$.[29]

state for the I_d mechanism could be found with more elaborate calculations involving a second coordination sphere represented by at least 10 water molecules. In such a model compound, the exchanging OH_2 ligands could not drift away easily to form H bonds because these H atoms would already be engaged in H bonds with the second coordination sphere. The present calculations indicate that transition states for the A, I_a, or I mechanisms are unlikely to be formed in the water exchange on $Ru(OH_2)_6^{2+}$.

It has been shown[38] for the water exchange on the aquapentaammineruthenium(III) ion that the geometries are quite insensitive to hydration, but for the calculation of at least qualitatively correct activation energies for several mechanistic pathways of a given reactant, the energy has to be computed by taking into account hydration. Thus, the activation energy for the water exchange on rhodium(III) via the interchange mechanism was found to be lower than that via the dissociative pathway (by ∼20 kJ/mol). Also, the change of the sum of all Rh−O bond lengths, $\Delta\Sigma d$(Rh−O) (eq 5), for the interchange mechanism is negative as the volume of activation. Thus, the calculations supply two parameters, the activation energy and $\Delta\Sigma d$(Rh−O), which both favor the interchange mechanism over the dissociative one.

For the $Ru(OH_2)_6^{2+}$ ion, only the D (or eventually the I_d) mechanism seems to be available on the basis of the present model.

Discussion

The usual approach to elucidate the mechanism of substitution reactions involves the study of the dependence of the reaction rate on reactants' concentration, pH, ionic strength, and solvent composition. For solvent exchange at metal ions these criteria are not applicable, and besides relying on theoretical simulation, one has to rely on the activation parameters obtained from variable temperature and pressure studies. In this context, the chief advantage of $\Delta V^‡$ measurements is that they are easily understood in terms of atomic movement alone; the interpretation of $\Delta S^‡$, on the other hand, involves fewer tangible factors such as molecular energy levels and the mode of occupation thereof. Volume changes on the macroscale are directly perceived by the human senses, whereas entropy is a transcendent abstraction; thus, one may theorize about $\Delta V^‡$, as suggested by Swaddle,[39] with much more confidence than in the cases of $\Delta S^‡$. It must also be recalled that for substitution reactions in general the experimentally determined $\Delta V^‡$ is usually discussed in terms of the sum of an intrinsic contribution, $\Delta V_{int}^‡$, arising from changes in the internuclear distances during the formation of the transition state, and an electrostrictive contribution, $\Delta V_{elec}^‡$. Fortunately, there is no overall charge creation or annihilation during a solvent exchange reaction, and for an octahedral aquaion in water, the change in dipole moment by going to the transition state will not produce a significant change in electrostriction. Therefore, in the cases of $Rh(OH_2)_6^{3+}$ and $Ru(OH_2)_6^{2+}$ the measured values are directly $\Delta V_{int}^‡$, or close to that parameter, and can be related to $\Delta\Sigma d$(M−O) (eq 5) and are available by computation (Table 1).

Attribution of the Exchange Mechanisms. (i) $Rh(OH_2)_6^{3+}$. The difference in the calculated activation energies, $\Delta E^‡$, for the water exchange on $Rh(OH_2)_6^{3+}$ via the interchange and the dissociative pathways is 21.8 kJ mol^{-1} in favor of the former (Figure 3). This argues against the D mechanism. Furthermore, the calculated $\Delta E^‡$ for the interchange mechanism is close to both experimental $\Delta G_{298}^‡$ and $\Delta H_{298}^‡$ values ($k^{298} = 2.2 \times 10^{-9}$ s^{-1}, $\Delta G_{298}^‡ = 122.3$ kJ mol^{-1}, $\Delta H_{298}^‡ = 131 \pm 23$ kJ mol^{-1}, $\Delta S_{298}^‡ = +29 \pm 69$ J K^{-1} mol^{-1}).

The experimental activation volume is −4.2 cm^3 mol^{-1} and supports the I_a mechanism. The computed $\Delta\Sigma d$(Rh−O) value of −0.534 Å (Table 1) argues also in favor of the I_a mechanism. Hence, the experimental and the computed data support the I_a mechanism for this exchange reaction.

Substitution or exchange reactions on the most extensively studied d^6 low-spin complexes, those of Co^{III} that are valence-isoelectronic with those of Rh^{III}, proceed via the I_d mechanism.[31,40] Because of the pronounced difference of these two electronically similar trivalent transition metal centers, the I_a mechanism for Rh^{III} will be analyzed in further detail and compared with the corresponding exchange reaction on $Rh(NH_3)_5OH_2^{3+}$.[41]

In the following it will be shown that the length of the Rh···O bonds in the transition state $[Rh(OH_2)_5\cdots(OH_2)_2{}^{3+}]^‡$ supports the I_a mechanism. The "normal" Rh−O bonds, for example, those in $Rh(OH_2)_6^{3+}$, are 2.066 Å, and as a value for an unbound OH_2 molecule in the second coordination sphere, the Rh···O bond length of 3.804 Å in the reactant $Rh(OH_2)_6\cdot OH_2^{3+}$ can be used (Table 1). The average of these two values, 2.935 Å, would indicate an approximate Rh···O bond length for the I mechanism. Since the calculated value of 2.700 Å is smaller, the I_a mechanism would again be attributed on the basis of this consideration (Figure 4).

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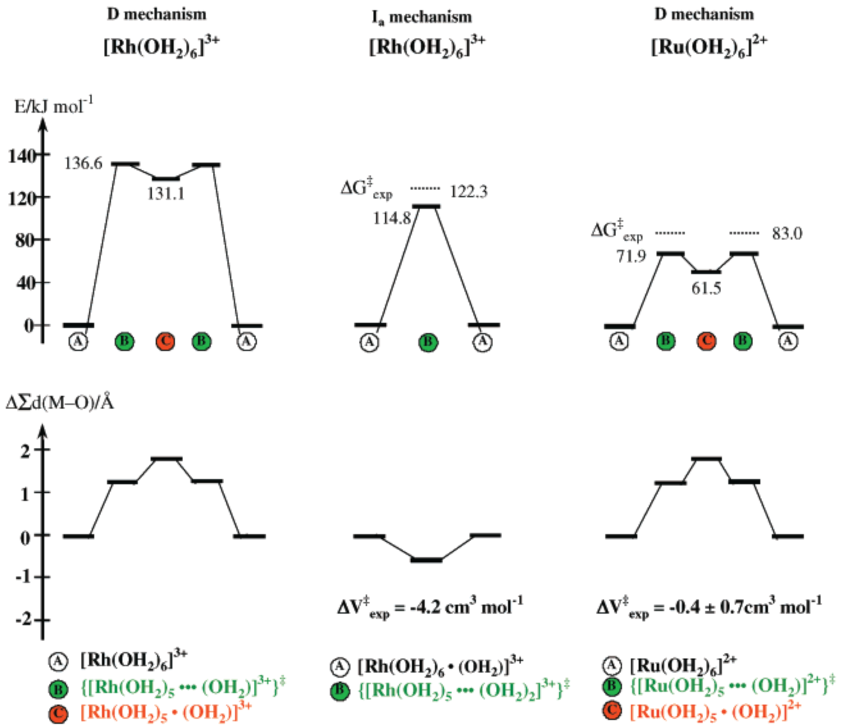

Figure 3. PCM energy $\Delta\Sigma d$(M−O)/Å (eq 5) and energy profiles for water exchange on rhodium(III) and ruthenium(II) hexaaquaions.

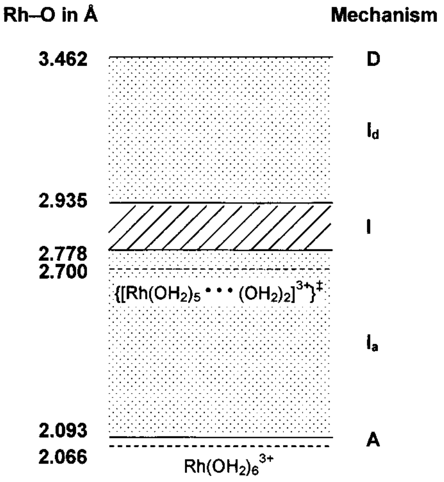

Figure 4. Water exchange on $Rh(OH_2)_6^{3+}$ showing the relation between possible mechanisms and calculated oxygen−metal distances at the corresponding transition states (in region bounded by - - -: Rh−O bond length for the hexaaquaion and the reacting water molecule for the I_a pathway).

Alternatively, we might define the Rh···O bond length for the I mechanism as the average of the bond length at the transition state for the D mechanism (3.462 Å) and for the A mechanism. As minimum value for the A mechanism, we may add to the hexaaquaion distance (2.066 Å) the equivalent of the bond shrinkage of the five Rh−O spectator bonds (0.027 Å) during the D activation process. This gives a Rh−O distance of 2.093 Å for the hypothetical A intermediate, itself shorter than the distance at the corresponding transition state. Therefore, the average gives a lower limit of 2.778 Å for the I mechanism. This limit is smaller than that calculated above but still allows us to conclude the presence of an I_a mechanism (Figure 4) that is close to the I pathway.

An additional argument in favor of the I_a mechanism can be obtained in comparison with the water exchange reaction on $Rh(NH_3)_5OH_2^{3+}$, which proceeds via the I mechanism.[41] The average Rh···O bond length in the transition state is 3.13 Å, and the corresponding $\Delta\Sigma d$(Rh−L) parameter is 0.01 Å, approximately zero. Clearly, both parameters, the Rh···O bond lengths and the $\Delta\Sigma d$(Rh−O) value for the water exchange on $Rh(OH_2)_6^{3+}$, are smaller than those for $Rh(NH_3)_5OH_2^{3+}$, and therefore once more, the I_a mechanism would be attributed preferentially to the water exchange process on $Rh(OH_2)_6^{3+}$. The longer Rh···O bonds in the transition state for the exchange reaction of $Rh(NH_3)_5OH_2^{3+}$ are due to the trans effect of the NH_3 ligand trans to the exchanging OH_2 molecules. The contribution of the cis NH_3 ligands is smaller.[42]

The steric course of this water exchange reaction is difficult, if not impossible, to study experimentally. According to the present calculations, the interchange pathway proceeds with retention of the configuration because the attack of the incoming water ligand takes place adjacent to the leaving ligand. In principle, the entering water could also attack opposite the leaving ligand, but this stereomobile pathway would require a much higher activation energy because it would involve a triplet electronic state. In the case of the water exchange on $Rh(NH_3)_5OH_2^{3+}$, the stereomobile pathway requires an activation energy that is higher by more than 100 kJ mol^{-1} than that with retention of the configuration.[41]

(ii) $Ru(OH_2)_6^{2+}$. All attempts to compute a transition state for an interchange mechanism failed because in such a (putative) transition state the Ru···O bonds are weaker than the hydrogen bonds with the equatorial water molecules. In the calculation starting with structures like those of Rh^{III}, the Ru···O bonds were elongated and then the OH_2 molecules drifted away toward the closest H atoms of the corresponding equatorial OH_2 ligands. The unavailability of a transition state for the I_d mechanism does not mean that it does not exist. It is just not available with the present model in which the second coordination sphere is not treated quantum chemically. The calculated $\Delta E^{\ddagger}$ for the D mechanism is also close to both experimental $\Delta G_{298}^{\ddagger}$ and $\Delta H_{298}^{\ddagger}$

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[42] Rotzinger, F. P. *J. Phys. Chem. A* **2000**, *104*, 8787−8795.

values ($k^{298} = 18 \times 10^3$ s^{-1}, $\Delta G_{298}^{\ddagger} = 83.0$ kJ mol^{-1}, $\Delta H_{298}^{\ddagger} = 87.8 \pm 4$ kJ mol^{-1}, $\Delta S_{298}^{\ddagger} = +16.1 \pm 15$ J K^{-1} mol^{-1}).[7] Therefore, the result of the present calculations suggests that water exchange on $Ru(OH_2)_6^{2+}$ proceeds via a “d” activation, either the I_d or the D mechanism. This result is in agreement with a high-pressure study of the formation of $[Ru(OH_2)_5\text{-}DMF]^{2+}$ from the aquaion for which the volume of the transition state is between the volume of the reactant and the volume of the products; an I_d mechanism has been assigned.[11]

Finally, the suggestion that the abnormally small observed $\Delta V^{\ddagger}$ value of -0.4 ± 0.7 cm^3 mol^{-1} could be due to the contraction of the bonds between Ru and the spectator ligands merits a comment. The calculation for the D mechanism shows an average shortening of 0.026 Å of the bond to the spectator water molecules, from 2.209 to 2.183 Å for the Ru−O distance at the transition state (Table 1). Translating this contraction to $^5/_6$ of the volume of $Ru(OH_2)_6^{2+}$ enclosed in a Connolly sphere[43] with a radius probe of 1.4 Å ($V = 85.67$ cm^3 mol^{-1}) gives a value of -1.7 cm^3 mol^{-1}. This would leave approximately $+1-2$ cm^3 mol^{-1} for the volume increase due to the bond rupture of the leaving water molecule. The estimated value due to the bond lengthening of 1.380 Å to reach the transition state is clearly larger but may be compensated by the negative contribution of the entering water molecule in an I_d process. Interestingly for $Rh(OH_2)_6^{3+}$, an already more compact ion because of its +3 charge, the bond shortening of the spectator ligands is the same (0.027 Å) for the hypothetical D mechanism; the higher positive charge than for Ru^{II} cannot promote further volume contraction in forming the pentaaqua transition state to change the sign of $\Delta V^{\ddagger}$ to a negative value. Furthermore, the contraction is definitively smaller (0.013 Å) for the operating I_a mechanism on $Rh(OH_2)_6^{3+}$ ($V = 81.83$ cm^3 mol^{-1}). To this small change corresponds a volume decrease of maximum 0.8 cm^3 mol^{-1}.

Conclusion

Why do the hexaaquaaions of Rh^{III} and Ru^{II} undergo water exchange via disparate mechanisms although they are isoelectronic? The charges are different, especially the M−O *bond strengths*. This is manifested by the activation energies for the exchange reactions via the D mechanism (Figure 3); for Rh^{III}, $\Delta E^{\ddagger}$ is equal to 136.6 kJ/mol, whereas for Ru^{II}, $\Delta E^{\ddagger}$ is about half that value, namely, 71.9 kJ/mol. The Rh^{III}−O bonds are considerably stronger than the Ru^{II}−O bonds, and the same holds also for the corresponding M···O bonds in the transition state for the interchange mechanism. Because of the strong Rh^{III}−O bonds, water exchange on $Rh(OH_2)_6^{3+}$ proceeds via the I_a pathway (close to I), whereas the same reaction of $Ru(OH_2)_6^{2+}$, which has considerably weaker Ru^{II}−O bonds, follows the I_d or the D mechanism.

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Supporting Information Available: A listing of the total energies and atomic coordinates of all reactants/products, transition states, and pentacoordinated intermediates (Tables S1−S8). This material is available free of charge via the Internet at http://pubs.acs.org.

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[43] Connolly, M. L. *J. Appl. Crystallogr.* **1983**, *16*, 548−558.