

Mechanism of Water Exchange for the Di- and Trivalent Metal Hexaaqua Ions of the First Transition Series

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Abstract: The mechanism for the water-exchange reaction with the transition metal aqua ions from Sc^{III} through Zn^{II} has been investigated. The exchange mechanisms were analyzed on the previously reported model (Rotzinger, F. P. *J. Am. Chem. Soc.* **1996**, *118*, 6760) that involves the metal ion with six or seven water molecules. The structures of the reactants/products, transition states, and penta- or heptacoordinated intermediates have been computed with Hartree–Fock or CAS-SCF methods. Each type of mechanism, associative, concerted or dissociative, proceeds via a characteristic transition state. The calculated activation energies agree with the experimental ΔG^\ddagger_{298} or ΔH^\ddagger_{298} values, and the computed structural changes indicate whether an expansion or compression takes place during the transformation of the reactant into the transition state. These changes are in perfect agreement with the changes deduced from the experimental volumes of activation (ΔV^\ddagger_{298}). The motions of the ligands involved in the exchange reaction are described by the imaginary vibrational mode. All these computed quantities allow the attribution of the water-exchange reactions to the A, I_a, or D mechanisms with use of the terminology of Merbach (Merbach, A. E. *Pure Appl. Chem.* **1982**, *54*, 1479). Within the present model, no transition state has been found for the I_d mechanism. It remains to be verified, using an improved model, whether it really does not exist. The dissociative mechanism is always feasible, but it is the only possible pathway for high-spin d⁸, d⁹, and d¹⁰ systems. In contrast, the associative mechanism requires that the transition metal ion does not have more than seven 3d electrons. Thus, Sc^{III}, Ti^{III}, and V^{III} react via the A, Ni^{II}, Cu^{II}, and Zn^{II} via the D (or I_d) mechanism, whereas for the elements in the middle of the periodic table, the high-spin 3d³–3d⁷ systems, both associative (I_a/A) and dissociative (D) pathways are feasible. The present results suggest that for Sc^{III} hexa- and heptacoordinated species could coexist in aqueous solution.

Introduction

Ligand substitutions and exchange involving a variety of metal ions, main group elements, and ligands have been reviewed recently by Lincoln and Merbach.¹ The most simple substitution process involving aqua complexes of transition metals is the water exchange. The detailed knowledge of such reactions is, however, relevant not only for the understanding of the substitution mechanisms but also for the electron transfer proceeding via the inner-sphere pathway, since the latter is necessarily preceded by a substitution process.²

The substitution mechanisms were classified by Langford and Gray³ with the symbols A, I_a, I_d, and D, where A and D represent associative and dissociative mechanisms proceeding via hepta- or pentacoordinated intermediates, respectively. I_a describes concerted reactions that have associative character, and I_d represents concerted processes with dissociative character. The distinction³ of A and I_a or D and I_d mechanisms is based on the experimentally measurable selectivity of the intermediates. For example, in a D process, the *product distribution* is altered upon the addition of nucleophiles, but the *rate* of the reaction remains unchanged. The selectivity of the pentacoordinated intermediates is measurable, if their lifetime is greater than the time required for the reorganization of its contact solvation shell, the second coordination sphere for the present

systems. Recently, Bleuzen et al.⁴ have investigated the exchange of water in the second coordination sphere of Cr(OH₂)₆³⁺: its residence time is 128 ps. Intermediates with a longer lifetime are detectable experimentally, whereas those with a shorter lifetime are not and undergo therefore a substitution following the I_d mechanism. These selectivity criteria are, however, not applicable to associative reactions.³ In 1982, Merbach⁵ introduced a different definition for the interchange mechanisms, where concerted ligand-exchange reactions proceed via a *single and symmetrical transition state*. The I_a and I_d pathways do not involve any intermediate: for I_a, bond formation dominates the activation process, whereas for I_d, it is bond breaking. This definition, being based on structural criteria, is adopted in the present study. Moreover, dissociative reactions proceeding via a pentacoordinated intermediate, even if it is short-lived and experimentally undetectable, will be considered as D processes.

The volume of activation (ΔV^\ddagger) is generally accepted to be the strongest criterion for the attribution of the mechanism of exchange reactions: large negative values point toward an A and large positive values toward a D mechanism.⁶ Smaller values are interpreted as a concerted mechanism. All these activation parameters describe global or total phenomena, viz. every parameter describes the sum of the effects arising from the bulk solvent, the solvent of the second coordination sphere, and the transition metal complex itself. For water exchange, the contribution due to the *change* of electrostriction of the second coordination sphere and bulk water is known to be small.⁵ Therefore, the experimental ΔV^\ddagger values reflect mainly

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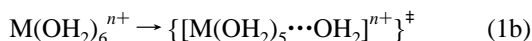
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changes in the first coordination sphere, and those are investigated with the present calculations.

Because of the unavailability of unequivocal criteria for the assignment of substitution mechanisms in octahedral transition metal complexes, the usefulness of the Langford–Gray classification³ has been questioned,⁷ and a mechanistic continuum of the interchange type proposed. The present results that are, however, based on a rather simple model supply evidence for the existence of both concerted (I_a) and two-step (A, D) mechanisms.

In a previous study,⁸ the water-exchange mechanism for the associative, concerted, and dissociative pathways has been investigated by using *ab initio* methods. It has been shown that each type of mechanism proceeds via a characteristic transition state, such that its structure allows the identification of the substitution mechanism. As representative examples for the three classes of mechanisms, the water exchange of the hexaaqua ions of Ti^{III} , V^{II} , and Ni^{II} has been analyzed⁸ in detail.

Water exchange proceeding via the associative or concerted pathway involves the participation of a seventh water molecule. The previously described model⁸ is based on the reaction involving the monohydrates of the hexaaqua ions in the gas phase, $[M(OH_2)_6 \cdot OH_2]^{n+}$, and it allows the computation of activation energies based on eq 1. Equation 1b, however, is applicable only to dissociative processes.



In this relatively simple model, the entire second coordination sphere except one water molecule, the anions, and also the bulk solvent have been neglected; gas-phase species with the composition of $M(OH_2)_7^{n+}$ or $M(OH_2)_6^{n+}$ have been investigated. Since the zero-point energy is expected to be small compared with that arising from the above approximations, it has been neglected throughout.

It has been shown previously⁸ that the neglect of dynamic electron correlation yields slightly longer M–O bond lengths. The omission of anions and water in the second coordination sphere, however, is more severe and leads to a larger error, also an elongation of the M–O bonds. All these approximations and limitations have already been discussed. It should be noted that because of the simplicity of this model, the present mechanistic inferences should not be considered as definitive.

The lifetime (τ) of the penta- and heptacoordinated intermediates being formed in the exchange via the D or A mechanism, respectively, has been calculated based on reaction 2 and eq 3,⁹ where ΔE_1^\ddagger represents the activation energy of reaction 2.



$$\tau = 1/k; \quad k = Z \exp\{-\Delta E_1^\ddagger/RT\}; \quad Z \approx 10^{11} \text{ s}^{-1} \quad (3)$$

The application of the above model required the computation of the structures of the reactants/products, transition states, and intermediates. These structures have been correlated with the experimentally determined volumes of activation (ΔV^\ddagger): the change of the sum of all the M–O bond lengths ($\Delta \Sigma$) during the activation process has been computed, and the sign of $\Delta \Sigma$ agrees with that of ΔV^\ddagger . Hence, the computed structural changes supply an additional criterion for the assignment of the mechanism.

The present study reports on the water exchange of all the first row transition elements with a 2+ and 3+ charge except $Co(OH_2)_6^{3+}$. All the pertinent transition states and intermediates have been computed, and the present model was found to be applicable to all these water-exchange reactions. No new transition states or intermediates have been found, but there are slight structural variations of the previously⁸ described structures. The average deviation of calculated (ΔE^\ddagger) and experimental (ΔG_{298}^\ddagger) energies of activation is 3.2 kJ/mol—the maximum deviation being 10.7 kJ/mol (for V^{III}). The sign of all the computed $\Delta \Sigma$ values agrees with that of the available ΔV_{298}^\ddagger values.^{1,10}

The lifetime of all the intermediates has been computed based on eqs 2 and 3 and gives further insight into the A and D mechanisms. Finally, the required electronic conditions that must be met for a given pathway to be feasible and the correlation between the electronic structure of the metal and the preferred pathways are discussed.

In contrast to Åkesson et al.'s findings,¹¹ the present calculations favor an associative water-exchange mechanism for Mn^{II} . The same disagreement has already been found for V^{II} in an earlier work.⁸ The present results on all the first row transition elements, in particular V^{II} and Mn^{II} , agree with the mechanisms assigned on the basis of experimentally determined^{1,10} volumes of activation.

Results

For the water exchange of all the 2+ and 3+ charged first row transition elements, the reactant/product, transition state, and intermediate structures have been calculated for the associative, concerted, and dissociative substitution mechanisms by using Hartree–Fock or CAS-SCF methods. Each of the three pathways proceeds via a characteristic transition state, which is represented by the water exchange involving Ti^{III} , V^{II} and Ni^{II} , respectively, proceeding via the associative, concerted, and dissociative mechanisms.⁸ In the present investigation of all the other first row transition elements, no new structures have been found, although slight deviations from the previously reported ones exist. The latter are typical for a given mechanism. For some transition metals, the D mechanism proceeding via a trigonal bipyramidal transition state and intermediate might be preferred over the corresponding square pyramidal species. This has already been observed by Åkesson et al.¹¹

The total energies, the electronic states, and the sum of all the M–O bond lengths including the M–O distances to water molecules of the second coordination sphere, $\sum d(M-O)$, for the various reactants/products, transition states, and intermediates (except the previously published⁸ Ti^{III} , V^{II} , and Ni^{II}) are reported in Table S1 (see Supporting Information). The computed activation energies (ΔE^\ddagger) for the associative, concerted, and dissociative pathway, computed according to eq 1, together with the corresponding differences of the $\sum d(M-O)$ values, $\Delta \Sigma$, are summarized in Table 1, where for comparison the experimental ΔG_{298}^\ddagger , ΔH_{298}^\ddagger , and ΔV_{298}^\ddagger values were also included. The relationship between ΔE^\ddagger and ΔG_{298}^\ddagger or ΔH_{298}^\ddagger has been discussed previously.⁸ The blank entries indicate that the particular mechanism does not exist (within the present model at least) for the corresponding metal.

In the following sections, the results for the associative, concerted, and dissociative pathways will be presented in detail.

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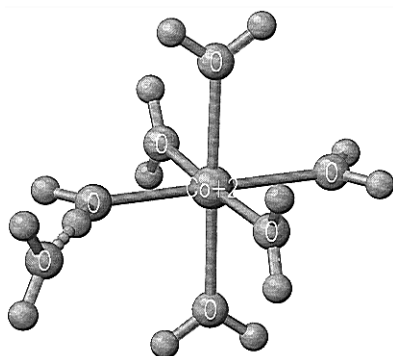
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Table 1. Activation Energies for the Various Exchange Mechanisms

metal	$\Delta E_{\text{calc}}^{\ddagger a}$ ($\Delta \Sigma$, Å)			exptl values (25 °C)	
	A	I _a	D ^b	ΔG^{\ddagger} , $\Delta H^{\ddagger a,c}$	$\Delta V^{\ddagger c,d}$
Sc ^{III}	22.3 (−1.11)		>89.5 ^e		
Ti ^{III}	35.2 (−1.22) ^f		>91.2 ^{e,f}	43.0, 43.4	−12.1
V ^{III}	47.0 (−1.22)		>93.6 ^e	57.7, 49.4	−8.9
V ^{II}		57.9 (−1.18) ^f	58.0 (+1.27) ^f	61.9, 61.8	−4.1
Cr ^{III}		98.2 (−1.20)	120.9 (+1.21)	105, 109	−9.6
Cr ^{II}		29.8 (−1.19)	15.9 (+1.74)	≈24–31 ^g	+4.3 ^g
Mn ^{III}		60.7 (−1.17)	54.1 (+0.90) ^e		
Mn ^{II}	30.9 (−1.49)		32.4 (+0.75), 32.4 (+0.93) ^e	31.2, 32.9	−5.4
Fe ^{III}	58.8 (−1.35)		>74.8 ^e	60.4, 64.0	−5.4
Fe ^{II}		42.3 (−1.52)	34.8 (+0.74)	35.1, 41.4	+3.8
Co ^{II}	45.9 (−1.50)		38.0 (+0.78)	35.8, 46.9	+6.1
Ni ^{II}			46.9 (+1.08) ^f , 42.9 (+1.00) ^{e,f}	47.4, 56.9	+7.2
Cu ^{II}			19.8 (+0.73), 17.6 (+0.70) ^e	21.9, 24.3 ^h	+2.0 ^h
Zn ^{II}			27.3 (+0.66)		

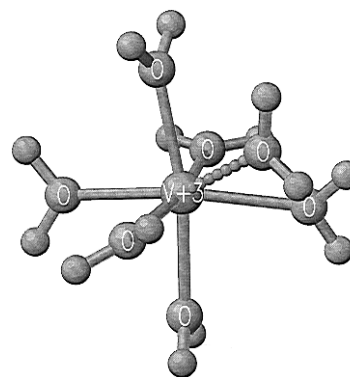
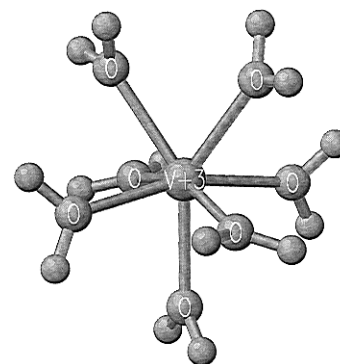
^a Units: kJ/mol. ^b Calculated according to eq 1b, unless noted otherwise. ^c Reference 1. ^d Units: cm³/mol. ^e Calculated according to eq 1a. ^f Reference 8. ^g Reference 12, ΔG^{\ddagger} at 20 °C. ^h Reference 10.

**Figure 1.** Perspective view of the water adduct $[\text{Co}(\text{OH}_2)_6 \cdot \text{OH}_2]^{2+}$.

Several structural varieties exist for the water adducts $[\text{M}(\text{OH}_2)_6 \cdot \text{H}_2\text{O}]^{n+}$: the seventh water molecule may be hydrogen bonded to one ligand, or it may bridge two ligands of the first coordination sphere. In order to treat all the transition metals in a uniform way, the previously⁸ introduced species (Figure 1) were used as reactants. Several electronic states have been computed for the various species, but only the most stable ones are reported. The reactions starting from the other isomer with a bridging water molecule in the second coordination sphere have not been investigated.

Associative Mechanism. This pathway has been analyzed⁸ in detail for the water exchange of $\text{Ti}(\text{OH}_2)_6^{3+}$. It is also feasible for Sc^{III}, V^{III}, Mn^{II}, Fe^{III}, Co^{II} (Tables S1 and 1), and the doublet states of Cr^{III} which will not be discussed; they resemble those of V^{II}.⁸ The transition states for the associative water exchange involving all these metal ions exhibit C_1 symmetry and very similar structures, although the M–O bond lengths may vary considerably (Table S1). As a representative example, the structure of the transition state $\{[\text{V}(\text{OH}_2)_6 \cdots \text{OH}_2]^{3+}\}^{\ddagger}$ is shown in Figure 2; the entering (or leaving) water molecule is readily visible. As in the case of Ti^{III}, the imaginary mode describes the motion of the incoming or leaving water molecule. These energies of activation have been computed with use of eq 1a (Table 1).

The heptacoordinated intermediate formed in the water exchange of $\text{Ti}(\text{OH}_2)_6^{3+}$ has C_1 symmetry,⁸ whereas that of Sc^{III}, V^{III}, Mn^{II}, Fe^{III}, and Co^{II} is C_2 . The pertinent energies and M–O bond lengths are given in Table S1, and as an example, the structure of the intermediate $\text{V}(\text{OH}_2)_7^{3+}$ is shown in Figure 3. The energy of activation for the decomposition of the intermedi-

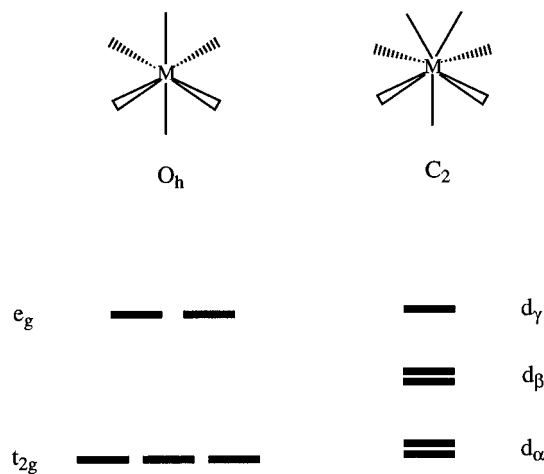
**Figure 2.** Perspective view of the transition state $\{[\text{V}(\text{OH}_2)_6 \cdots \text{OH}_2]^{3+}\}^{\ddagger}$ formed via the A mechanism.**Figure 3.** Perspective view of the heptacoordinated intermediate $\text{V}(\text{OH}_2)_7^{3+}$.

ates (ΔE_1^{\ddagger} , eq 2) and their lifetimes are reported in Table 2. Relatively long-lived intermediates are formed by Sc^{III}, Ti^{III}, and V^{III}, whereas those of Mn^{II}, Fe^{III}, and Co^{II} are very short lived. A qualitative diagram of the (Hartree–Fock) orbital energies of hexacoordinated high-spin $3d^5$ $\text{M}(\text{OH}_2)_6^{n+}$ species with T_h symmetry and their corresponding heptacoordinated analogs with C_2 symmetry, e.g. $\text{Mn}(\text{OH}_2)_7^{2+}$ or $\text{Fe}(\text{OH}_2)_7^{3+}$, having each 3d orbital occupied by a single electron, is shown in Figure 4. In contrast to the hexacoordinated species with three nonbonding 3d levels (t_g), the heptacoordinated ones, $\text{M}(\text{OH}_2)_7^{n+}$, exhibit two nonbonding and nearly degenerate (d_α), two slightly antibonding and nearly degenerate (d_β), and one strongly antibonding (d_γ) 3d orbitals. Transition metals in which only the nonbonding levels are occupied, for example, $3d^0$, $3d^1$,

Table 2. Calculated Energy and Lifetime of the Heptacoordinated Intermediates

metal	$\Delta E,^a$ kJ/mol	$\tau,^b$ ns	$\Delta E_1^\ddagger,^c$ kJ/mol
Sc ^{III}	0.5	66	21.8
Ti ^{III}	22.1	2.0	13.1
V ^{III}	34.9	1.3	12.1
Mn ^{II}	28.8	0.023	2.1
Fe ^{III}	55.5	0.038	3.3
Co ^{II}	45.6	0.010	0.3

^a $\Delta E = E\{M(OH_2)_7^{n+}\} - E\{[M(OH_2)_6 \cdot OH_2]^{n+}\}$. ^b Estimation based on eq 3. ^c Reaction 2.

**Figure 4.** Qualitative orbital diagram for hexa- and heptacoordinated first row transition metal complexes.

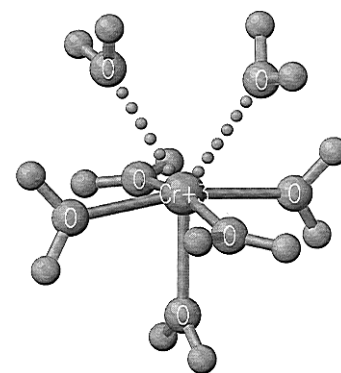
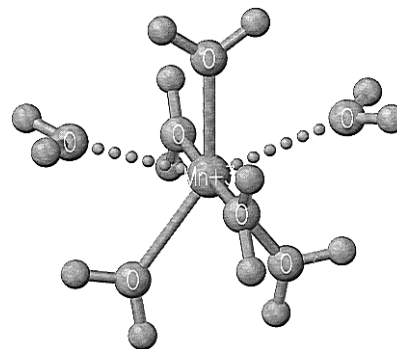
high-spin $3d^2$, and low-spin $3d^3$ and $3d^4$ systems, form the most stable and therefore longer-lived heptacoordinated species. Their favorable electronic structure suggests that the systems having only the d_α levels occupied react preferentially via the A mechanism.

The heptacoordinated intermediates $Mn(OH_2)_7^{2+}$, $Fe(OH_2)_7^{3+}$, and $Co(OH_2)_7^{2+}$ exhibit symmetric electronic structures with respect to the orbital diagram shown in Figure 4 and, in addition to the d_α shell occupied by two or four electrons, all the d_β and d_γ levels are occupied each by one electron. Table 2 shows that for these systems, the transition state energies are very close to those of their corresponding intermediates and, consequently, their lifetimes are much shorter than those of Sc^{III}, Ti^{III}, and V^{III}.

The occupation of the d_α levels determines also the symmetry of the heptacoordinated species: a symmetric occupation, for example d^0 (Sc^{III}) or high-spin $3d^2$ (V^{III}), gives rise to species with C_2 symmetry, whereas an asymmetric population, for example, $3d^1$ (Ti^{III})⁸ or low-spin $3d^3$ (doublet states of V^{II})⁸ lowers the symmetry to C_1 .

In Table 2 are also reported the energies of the heptacoordinated intermediates in comparison to those of the hexacoordinated water adducts $[M(OH_2)_6 \cdot OH_2]^{n+}$. Interestingly, the energy of heptacoordinated Sc(OH₂)₇³⁺ is almost identical with that of its corresponding water adduct. This result suggests that hexa- and heptacoordinated Sc^{III} species may coexist in aqueous solution.

Concerted Mechanism. The example of the water exchange of $V(OH_2)_6^{2+}$ has already been investigated in detail.⁸ The hexaqua ions of Cr^{III} and Fe^{II} react similarly (Cr^{III} is isoelectronic with V^{II}). For these metals, the transition states have the entering and leaving water molecule in the *cis* position to each other. They exhibit C_2 symmetry and strongly resemble the heptacoordinated intermediates (Figure 3). As an example, the structure of $\{[Cr(OH_2)_5 \cdots (OH_2)_2]^{3+}\}^\ddagger$ is depicted in Figure

**Figure 5.** Perspective view of the transition state $\{[Cr(OH_2)_5 \cdots (OH_2)_2]^{3+}\}^\ddagger$ formed via the I_a mechanism.**Figure 6.** Perspective view of the nearly pentagonal bipyramidal transition state $\{[Mn(OH_2)_5 \cdots (OH_2)_2]^{3+}\}^\ddagger$ formed via the I_a mechanism.

5. The water exchange takes place via the displacement of one water molecule by the incoming ligand, while all the other five ligands remain relatively unchanged. In the case of Cr^{III}, the two elongated $M \cdots O$ bonds of the entering and leaving water ligands are clearly visible (Table S1 and Figure 5), whereas for Fe^{II}, the $M-O$ bond lengths of the “spectator” water ligands change during the water exchange.

Another isomer of the transition states for the concerted exchange mechanism exists. It also has C_2 symmetry, but in contrast to the above species (Figure 5), the entering and leaving ligands are not in the *cis* position to each other. The exchange takes place via the attack of the incoming ligand onto an edge of the MO_6 octahedron. The five equatorial water molecules rearrange by forming a nearly planar pentagon where one $M-O$ bond *trans* to the incoming ligand is weakened. The imaginary mode describes precisely this event. Such transition states could be formed in the water exchange involving the Jahn–Teller distorted isoelectronic hexaqua ions of Cr^{II} and Mn^{III}, and the structure of $\{[Mn(OH_2)_5 \cdots (OH_2)_2]^{3+}\}^\ddagger$ is shown in Figure 6. They resemble the previously described⁸ higher-order saddle points (exhibiting two imaginary frequencies) and also the heptacoordinated species described by Åkesson et al.¹¹ In the water exchange proceeding via these transition states, bond formation is more important than bond breaking (Table S1); the $\Delta\Sigma$ values (Table 1) are negative and of the same magnitude as for the above described transition states $\{[Cr(OH_2)_5 \cdots (OH_2)_2]^{3+}\}^\ddagger$ (Figure 5) and $\{[Fe(OH_2)_5 \cdots (OH_2)_2]^{2+}\}^\ddagger$. Therefore, these two types of transition states (Figures 5 and 6) arise from the water exchange via the I_a mechanism.

This type of transition state has also been obtained for V^{II} and Cr^{III}, but their energies are considerably higher (by more than 10 kJ/mol) than those of the transition states with the incoming and leaving ligands in the *cis* position. The nearly pentagonally bipyramidal species are more difficult to compute,

since they relaxed quite readily into the more stable transition states (Figure 5).

All the attempts to compute transition states corresponding to the I_d mechanism failed. This may be due to a limitation of the present model involving only seven water molecules. This point will be elaborated further in the discussion.

Dissociative Mechanism. The energy of activation for the water exchange proceeding via this mechanism can be computed by using either eq 1a or eq 1b. In addition to the preferred concerted I_a pathway for V^{II} , the dissociative pathway has been analyzed⁸ based on eq 1b. For Ni^{II} , the transition states have been computed by using both equations.⁸ All these species have C_s symmetry, and in the transition state $\{[Ni(OH_2)_5 \cdots OH_2 \cdot OH_2]^{2+}\}^\ddagger$ no indication for the entry of the water located in the second coordination sphere could be found. This indicates that within the present model (eq 1), no evidence for the I_d mechanism has been obtained.

In the present study, the dissociative water-exchange mechanism has been investigated for all the other first row transition metals. With the exception of Cr^{III} , the dissociation of water according to eq 1b involving complexes with a 3+ charge was found to occur concertedly, with the deprotonation of a water ligand in the equatorial plane, and the leaving water molecule acting as the proton acceptor. The products formed were H_3O^+ and a pentacoordinated hydroxo complex $M(OH)(OH_2)_4^{2+}$. This behavior is an artifact arising from the omission of anions and water in the second coordination sphere and was not observed for the 2+ charged complexes. Transition states that do not involve deprotonation could, however, be obtained with use of eq 1a. Such computations have been performed for the transition states of Mn^{III} , Mn^{II} , Ni^{II} ,⁸ and Cu^{II} (Tables S1 and 1) with C_s symmetry (labeled SQP1), where the metal ion has approximately a square pyramidal coordination sphere. As examples, the structures of $\{[Mn(OH_2)_5 \cdots OH_2 \cdot OH_2]^{2+}\}^\ddagger$ and $\{[Cu(OH_2)_5 \cdots OH_2 \cdot OH_2]^{2+}\}^\ddagger$ are shown in Figure 7. In contrast to Cu^{II} , Mn^{II} shows some tendency to form a trigonal bipyramid. The corresponding species of Sc^{III} , Ti^{III} , and V^{III} have not been computed, since the dissociative exchange is by no means competitive with the associative pathway (see below). In the transition state for the D mechanism, not a single structure has been found where the water molecule in the second coordination sphere shows any tendency to enter the first coordination sphere. In these species the M–O bond of the leaving group is stretched by about 1 Å (Figure 7).

For V^{II} , Cr^{III} , Cr^{II} , Mn^{II} , Fe^{II} , Co^{II} , Ni^{II} , Cu^{II} , and Zn^{II} the transition states were calculated based on eq 1b. Square pyramidal structures exhibiting C_s symmetry (abbreviated as SQP2) have been obtained for V^{II} , Cr^{III} , Cr^{II} , Ni^{II} , and Cu^{II} (Figure 8), whereas trigonal bipyramidal transition states (labeled TBP) were formed for Mn^{II} , Fe^{II} , Co^{II} , and Zn^{II} . The latter have C_{2v} symmetry, but for Fe^{II} , a transition state with C_s symmetry being more stable by 30.1 kJ/mol than its C_{2v} analog exists (Table S1). As examples, the structures of $\{[Mn(OH_2)_5 \cdots OH_2]^{2+}\}^\ddagger$ and $\{[Fe(OH_2)_5 \cdots OH_2]^{2+}\}^\ddagger$ are depicted in Figure 9.

The dissociation of the transition states $\{[M(OH_2)_5 \cdots OH_2 \cdot OH_2]^{n+}\}^\ddagger$ (SQP1 structure, Figure 7) leads to intermediates with C_{2v} symmetry as in the case of Ni^{II} . The calculations for Mn^{III} , Mn^{II} , Ni^{II} , and Cu^{II} are reported in Tables S1 and 1, and as examples, the corresponding species of Mn^{II} and Cu^{II} (arising from the decay of the transition states SQP1 shown in Figure 7) are depicted in Figure 10. The square pyramidal transition states (SQP2) involving V^{II} , Cr^{III} , Cr^{II} , Ni^{II} , and Cu^{II} form intermediates with C_s symmetry. The corresponding Cu^{II} species is represented in Figure 11. Interestingly, the pentacoordinated intermediates of the Jahn–Teller ions Cr^{II} and Cu^{II}

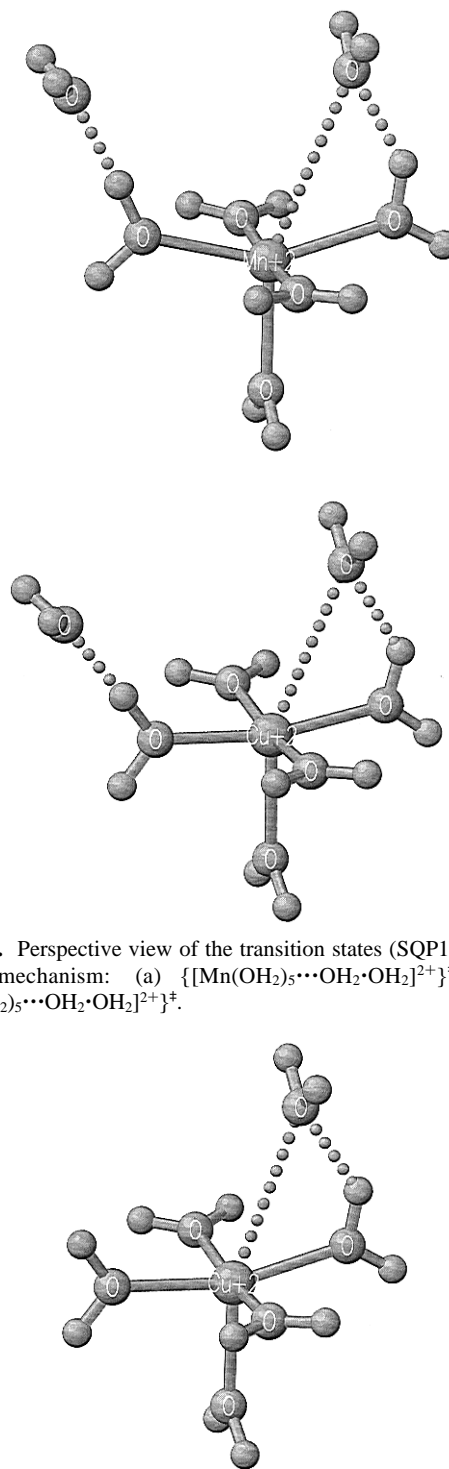


Figure 7. Perspective view of the transition states (SQP1) formed in the D mechanism: (a) $\{[Mn(OH_2)_5 \cdots OH_2 \cdot OH_2]^{2+}\}^\ddagger$ and (b) $\{[Cu(OH_2)_5 \cdots OH_2 \cdot OH_2]^{2+}\}^\ddagger$.

Figure 8. Perspective view of the square pyramidal transition state $\{[Cu(OH_2)_5 \cdots OH_2]^{2+}\}^\ddagger$ (SQP2) formed in the D mechanism.

are the least unstable ones (Table 3). This is obvious, because breaking of an elongated M–O bond is a facile process, especially if it is concerted with the compression of the corresponding *trans* M–O bond. The transition states with a trigonal bipyramidal structure (for Mn^{II} , Fe^{II} , Co^{II} , and Zn^{II} , viz. Figure 9) all lead to the corresponding intermediates with C_2 symmetry. For Fe^{II} , the intermediate with C_2 symmetry, arising from the decay of the unfavorable transition state having C_{2v} symmetry, is insignificantly (by -0.1 kJ/mol) more stable than that exhibiting C_s symmetry (Table S1). The latter arises from the decay of the lower energy transition state with C_s symmetry. The pertinent examples of Mn^{II} and Fe^{II} are shown in Figure 12.

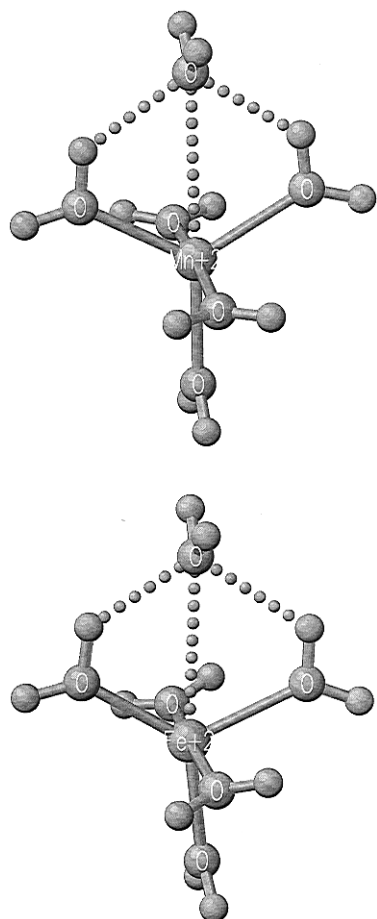


Figure 9. Perspective view of the trigonal bipyramidal transition states (TBP) formed in the D mechanism: (a) $\{[\text{Mn}(\text{OH}_2)_5 \cdots \text{OH}_2]^{2+}\}^\ddagger$ and (b) $\{[\text{Fe}(\text{OH}_2)_5 \cdots \text{OH}_2]^{2+}\}^\ddagger$.

The dissociative mechanism is possible for all the transition metals, but it requires a very high energy of activation for the elements on the left side of the periodic table (Sc^{III} , Ti^{III} , and V^{III}). The energy of the (hydrated) pentacoordinated intermediates, being slightly lower (by 5–10 kJ/mol, Table 3) than that of their corresponding transition states, is much higher than the activation energy required for the A mechanism (Tables S1 and 1). For this reason, these transition states, together with that of Fe^{III} , have not been computed.

Discussion

Attribution of the Mechanism. The reliability of the present calculations is established by the agreement of the computed activation energies ΔE^\ddagger and $\Delta \Sigma$ parameters with their respective experimental^{1,10} ΔG^\ddagger , ΔH^\ddagger , and ΔV^\ddagger values (Table 1). The computations supply structures and energies for a variety of transition states and intermediates arising from the water exchange of hexaaqua ions of the first row transition metals. Each type of mechanism, namely associative, concerted, and dissociative, proceeds via a characteristic transition state, and the three representative structures have already been described in previous work.⁸ The computed $\Delta \Sigma$ parameters reflect the total change of the bond lengths during the activation (reaction 1, Table 1), and the imaginary vibrational mode describes the motions of the water ligand(s) involved in the exchange reaction. The present computations supply criteria for the assignment of substitution mechanisms.

In the associatively activated exchange reaction (A mechanism), the entering water molecule attacks a face of the octahedron, distorting the latter slightly (Figure 2). The

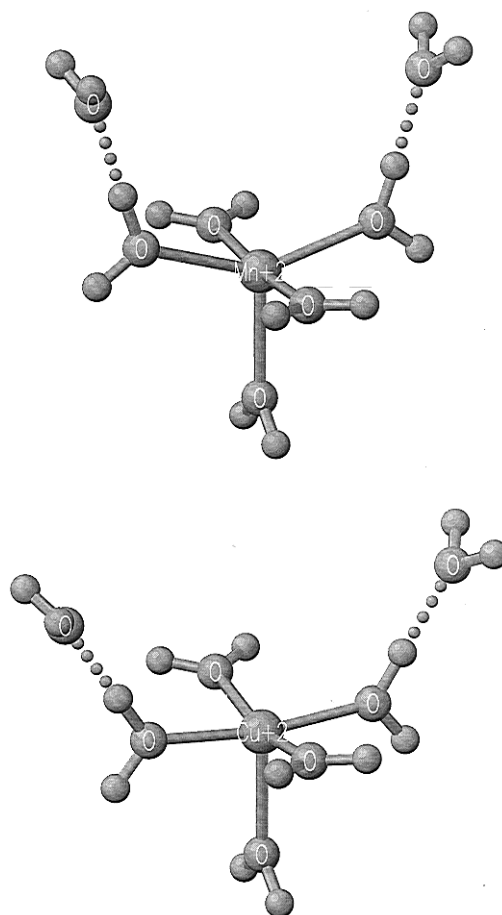


Figure 10. Perspective view of the pentacoordinated intermediates (SQP1) formed in the D mechanism: (a) $[\text{Mn}(\text{OH}_2)_5 \cdot (\text{OH}_2)_2]^{2+}$ and (b) $[\text{Cu}(\text{OH}_2)_5 \cdot (\text{OH}_2)_2]^{2+}$.

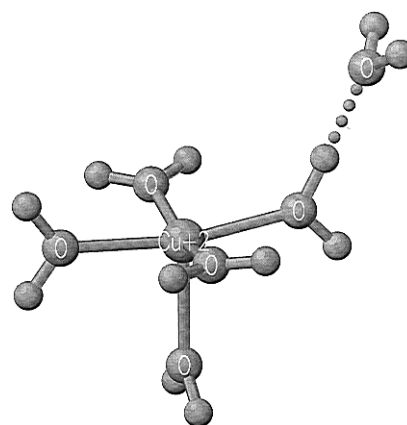


Figure 11. Perspective view of the pentacoordinated intermediate $[\text{Cu}(\text{OH}_2)_5 \cdot \text{OH}_2]^{2+}$ (SQP2) formed in the D mechanism.

pertinent $\Delta \Sigma$ values (Table 1) are negative and indicate that the transition state is reached by a compression of the reactant. In these transition states always having C_1 symmetry, the imaginary mode describes the motion of the entering (or leaving) ligand toward or away from the metal center. The incoming ligand exhibits a $\text{M} \cdots \text{O}$ bond length that is significantly longer than those of the six others (Table S1). Such transition states, exhibiting six normal (or slightly elongated) $\text{M}-\text{O}$ bonds and one long (weak) $\text{M} \cdots \text{O}$ bond, have been found for Sc^{III} , Ti^{III} , V^{III} , Mn^{II} , Fe^{III} , and Co^{II} . The subsequently formed hepta-coordinated intermediates (Figure 3), having either C_2 or C_1 symmetry (see Associative Mechanism in the Results section),

Table 3. Calculated Energy and Lifetime of the Pentacoordinated Intermediates

metal	ΔE , kJ/mol	τ , ns	ΔE_1^\ddagger , kJ/mol	species ^a
V ^{II}	56.7	0.017	1.3	SQP2
Cr ^{III}	117.3	0.043	3.6	SQP2
Cr ^{II}	11.1	0.069	4.8	SQP2
Mn ^{III}	45.7	0.30	8.4	SQP1
Mn ^{II}	28.6	0.046	3.8	SQP1
	25.9	0.140	6.5	TBP
Fe ^{II}	23.1	1.12	11.7	TBP
Co ^{II}	30.6	0.20	7.4	TBP
Ni ^{II}	43.4	0.041	3.5	SQP2
	38.2	0.067	4.7	SQP1
Cu ^{II}	13.5	0.13	6.3	SQP2
	9.4	0.27	8.2	SQP1
Zn ^{II}	18.9	0.30	8.4	TBP

^a SQP1: square pyramidal transition state $\{[M(OH_2)_5 \cdots OH_2 \cdot OH_2]^{n+}\}^\ddagger$.
 SQP2: square pyramidal transition state $\{[M(OH_2)_5 \cdots OH_2]^{n+}\}^\ddagger$. TBP:
 trigonal bipyramidal transition state $\{[M(OH_2)_5 \cdots OH_2]^{n+}\}^\ddagger$.

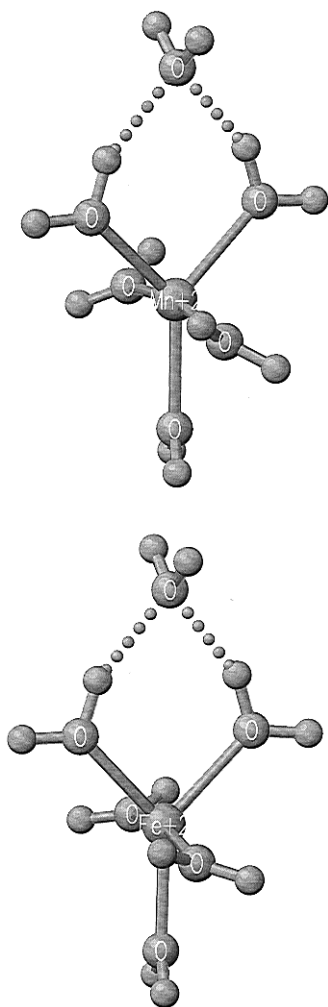


Figure 12. Perspective view of the trigonal bipyramidal intermediates (TBP) formed in the D mechanism: (a) $[Mn(OH_2)_5 \cdot OH_2]^{2+}$ and (b) $[Fe(OH_2)_5 \cdot OH_2]^{2+}$.

have slightly longer average M—O bond lengths than the hexacoordinated reactants.

For the second type of transition state, the associative interchange mechanism (I_a), two structurally different species, each with C_2 symmetry, have been obtained. The two structures arise either from the attack in the *cis* (Figure 5) or the *trans* (Figure 6) position to the leaving ligand. The former has been found for V^{II},⁸ Cr^{III}, and Fe^{II}, and the latter for Cr^{II} and Mn^{III}. Both types of transition states, exhibiting five normal M—O

bonds and two long symmetrically equivalent $M \cdots O$ bonds, are representative for the I_a mechanism, since bond formation occurs to a larger extent than bond breaking as shown by the calculated $\Delta\Sigma$ values (Table 1). The imaginary mode describes a concerted motion of the two weakly bound water ligands, where one bond is shortened and the other one elongated correspondingly. Within the present model, no transition state for the I_d mechanism has been found.

In the third type of transition state, dissociative activation (D), the $M \cdots O$ bond of the leaving ligand is elongated by about 1 Å. The corresponding $\Delta\Sigma$ values are positive (Table 1), and this transition state is characterized by five normal M—O and one long $M \cdots O$ bonds. The imaginary mode describes the motion of the activated ligand toward or away from the metal center. Ligand loss is concerted with the rearrangement to a trigonal bipyramidal structure exhibiting C_{2v} symmetry for Mn^{II}, Co^{II}, and Zn^{II} (Figure 9a) and C_s or C_{2v} symmetry for Fe^{II} (Figure 9b). This rearrangement is only possible for specific occupations of the 3d levels and will be discussed in the next section. The presence of one water molecule in the second coordination sphere impedes this rearrangement (Figure 7), showing that the energies of the square pyramidal and trigonal bipyramidal structures are very close and dependent on the second coordination sphere. The corresponding pentacoordinated intermediates resemble their respective transition states very closely.

Although the present model, neglecting essentially all the solvent and the anions, is rather crude, it indicates that both concerted and two-step mechanisms exist. The transition states, together with their corresponding intermediates, can be attributed to the A, I_a , and D mechanisms.

Correlation of Mechanism and Electronic Structure. In agreement with Åkesson et al.'s findings,¹¹ the present computations indicate that the trigonal bipyramidal pentacoordinated intermediate is more stable for Mn^{II}, Fe^{II}, Co^{II}, and Zn^{II}, and the square pyramidal one is preferred for V^{II}, Cr^{III}, Cr^{II}, Mn^{III}, Ni^{II}, and Cu^{II}. This result is rationalized by decomposing conceptually the formation of a trigonal bipyramidal species into two steps, namely the dissociation of a water molecule from the hexacoordinated complex leading to the square pyramid, and the subsequent rearrangement of the latter to yield the trigonal bipyramid. Thus, the energy change upon rearrangement from square pyramid to trigonal bipyramid is the relevant parameter. It is analyzed by considering the occupation of the 3d levels of the hexaaqua ions. As an example, the dissociation of a water molecule lying on the *z* axis of a $M(OH_2)_6^{n+}$ complex is discussed. The primary product, the square pyramid, may then transform into the trigonal bipyramid. This involves the motion of two (*trans* to each other) of the four water molecules out of the *xy* plane in the same direction as the leaving ligand. This motion is unfavorable, if the occupation of the $d_{x^2-y^2}$ orbitals is lower than each of the d_{xz} , d_{yz} pair. In this case, the d_{xz} , d_{yz} orbitals can be considered as an electronic barrier for the motion of the two M—O bonds (each exhibiting 2 electrons) into the *z* direction. The following examples illustrate the above model: In the case of $V(OH_2)_6^{2+}$ or $Cr(OH_2)_6^{3+}$ the water ligand on the (positive) *z* axis is removed. The $d_{x^2-y^2}$ (and d_z^2) orbital is empty, whereas the d_{xz} , d_{yz} (and d_{xy}) orbitals are each occupied by one electron. If the two equatorial water ligands would move into the *z* direction, one orbital of the d_{xz} , d_{yz} pair would become antibonding due to the interaction with the moving equatorial M—O bonds. At the same time, the $d_{x^2-y^2}$ orbital would be stabilized, but since the latter is empty, the rearrangement would lead to a rise in the total energy. If, however, the $d_{x^2-y^2}$ level is also occupied by a single electron, then the increase in energy

Table 4. Exchange Mechanism for the Transition Metal Hexaaqua Ions with 3dⁿ Electron Configurations

metal ion	<i>n</i>	mechanism ^a
Sc ^{III}	0	A
Ti ^{III}	1	A
V ^{III}	2	A
V ^{II} (doublet states)	3	A
Cr ^{III} (doublet states)	3	A
V ^{II}	3	I _a
Cr ^{III}	3	I _a
Cr ^{II}	4	D
Mn ^{III}	4	D (or I _a ?) ^b
Mn ^{II}	5	A (or I _a ?) ^b
Fe ^{III}	5	A (or I _a ?) ^b
Fe ^{II}	6	D
Co ^{II}	7	D
Ni ^{II}	8	D
Cu ^{II}	9	D
Zn ^{II}	10	D

^a It remains to be checked, using an improved model, whether some (or all?) of the reactions to which the D mechanism has been assigned proceed, in fact, via I_a. ^b See text.

of one orbital of the d_{xz}, d_{yz} pair would be compensated by the stabilization of the d_{x²-y²} level. This situation applies for Mn^{II} which indeed rearranges. In the case of Ni^{II}, the d_{xz}, d_{yz} pair is occupied by four electrons and the d_{x²-y²} orbital by one. The rearrangement does not take place, since the destabilization of a doubly occupied orbital (d_{xz} or d_{yz}) cannot be counterbalanced by the stabilization of a singly occupied level (d_{x²-y²}). The latter is doubly occupied in Zn^{II}, and therefore, in this case, the rearrangement is possible and indeed occurs.

The above model predicts that trigonal bipyramidal intermediates could also be formed for the unfavorable dissociative exchange reactions of Sc^{III}, Ti^{III}, V^{III}, and Fe^{III}. In fact, Åkesson et al.¹¹ have shown that these are indeed the preferred intermediates for Ti^{III}, V^{III}, and Fe^{III}.

The preference for a mechanism is rationalized by analyzing the electronic structure of the key species, the heptacoordinated intermediate or transition state. It has been shown in the Results section (Tables S1 and 1) that seven-coordinated transition states or intermediates should be formed preferentially by high-spin d⁰-d⁷ systems, but not the high-spin d⁸-d¹⁰ ones. The qualitative MO diagram (Figure 4) allows to understand why only high-spin systems with seven or less 3d electrons can form seven-coordinated species. There are, however, no straightforward criteria for the prediction of the nature of the seven-coordinated species exhibiting C₂ symmetry: its identification as an intermediate or transition state requires the computation of the vibrational frequencies. Of course, a given species cannot be an intermediate and transition state at the same time; for this reason, all the d⁰-d⁷ systems could undergo water exchange either via the A or the I_a mechanism and not via both (Table 1). For these systems, the I_d mechanism is impossible within the present model, because of the possibility of forming two relatively strong M···O bonds.

To summarize (Table 4), the A mechanism is favorable, when the heptacoordinated intermediate has empty d_β and d_γ levels (Figure 4). This is the case for Sc^{III}, Ti^{III}, and V^{III} and also for the doublet states of V^{II}⁸ and the isoelectronic Cr^{III}. The high-spin systems with 8–10 3d electrons, Ni^{II}, Cu^{II}, and Zn^{II}, do not form stable heptacoordinated species and react therefore via the D or eventually the I_d mechanism. The elements in the middle of the periodic table (high-spin 3d³-3d⁷ systems) can react either via an associative or a dissociative mechanism (Table 1). The I_a or A mechanism is preferred for metals with 3–5 3d electrons, and the D mechanism by those with 6 or 7 electrons. However, it should be noted that for the metal ions

with 3d³-3d⁷ electron configurations, the activation energies for the D and A/I_a mechanisms are close (Table 1). In these cases, the mechanism is very likely to be governed by the nature of incoming, leaving, and spectator ligands. In all cases, where the computed activation energies for the associative and dissociative exchange are close, the assignment of the mechanism was based on the sign of ΔΣ being in agreement with that of ΔV[‡]. Since the experimental volume of activation is not available for Mn^{III}, the exchange mechanism can in principle be predicted based on the computed ΔE[‡] values (Table 1), which favor water exchange via the D mechanism. Since, however, the present model is quite limited, it does not allow a safe prediction in this case. The activation energies for the D and I_a mechanisms are quite close, and therefore, the I_a pathway, requiring an only slightly higher activation energy (the difference is 6.6 kJ/mol), cannot be ruled out.

The present calculations show that the exchange mechanism depends on the electronic structure of the transition metal ion. The shortcoming of the hypothesis of the mechanistic continuum of the interchange type⁷ is that it does not take into account the occupation of the 3d levels of the metal and the widely applied concept of the ligand field stabilization energy (LFSE). The preference for the A and D mechanisms can be rationalized by using the LFSE's of the heptacoordinated species, using the qualitative orbital diagram represented in Figure 4.

Limitations of the Present Model. Water exchange proceeding via the A and D mechanisms involves hepta- or pentacoordinated intermediates, respectively, whose lifetimes have been calculated according to eq 3 (Tables 2 and 3). There are two types of heptacoordinated intermediates, long- and short-lived ones: relatively long lifetimes (of the order of 1–100 ns) have been computed for the early transition metals Sc^{III}, Ti^{III}, and V^{III}, and much shorter ones for Mn^{II}, Fe^{III}, and Co^{II} (<50 ps, Table 2). In relation to the limitations of the presently used model, the consequences for the assignment of the exchange mechanism are analyzed in the following paragraph.

Any improvement of the model, for example, the addition of a second coordination sphere, will change the energy of the intermediate and the transition state, most likely in an unequal manner. In all the cases where the energy difference between those two species is large, it is unlikely that despite an improvement of the model, the energy of the intermediate could become higher than that of the transition state (see below). Therefore, it is unlikely that another mechanism, for example the I_a one, would apply for Sc^{III}, Ti^{III}, and V^{III}, since the relatively large ΔE₁[‡] values (>10 kJ/mol) might in the worst case be reduced, but they are unlikely to turn negative (and convert the intermediate into a transition state). For this reason, the attribution of the A mechanism for the water exchange of Sc^{III}, Ti^{III}, and V^{III} should be safe.

The situation is, however, different for Mn^{II}, Fe^{III}, and Co^{II} where the energy gap between the transition state and the intermediate is small (<4 kJ/mol). Any improvement of the model could reduce this gap to zero, or make it negative. Then, the transition state based on the present model would no longer be a stationary point on the potential energy surface, and the intermediate (of the present model) would become the transition state. The mechanism would then have changed from A to I_a. The hexaaqua ions of Mn^{II} and Fe^{III} may thus well react via the I_a instead of the A mechanism, but Co^{II} anyway prefers a dissociative pathway (Table 4).

In general, the pentacoordinated intermediates are energetically close to their corresponding transition states (ΔE₁[‡] < 10 kJ/mol), and therefore, their lifetimes (being only a rough estimate, because of the limited model) are short (Table 3). As

for the associative case, it could be that for a dissociative activation, an improved model changes the energy of the pentacoordinated intermediate and its corresponding transition state in an unequal way, such that, as described above, the (hydrated) pentacoordinated intermediate becomes the transition state for the I_d mechanism. In the following paragraph, some reasons will be discussed why the latter does not seem to exist within the frame of the present model.

As already mentioned in the Results section, all attempts to compute a transition state for the I_d mechanism failed. This may be due to the limitations of the present model. Transition states for the I_d mechanism are expected to have the following properties: (i) In addition to the five M–O bonds with normal bond lengths, they should have two elongated M···O bonds in the range of that found in the transition state for the D mechanism (roughly 3.2 Å). These two bonds should, however, be significantly shorter than those of water molecules in the second coordination sphere. (ii) The normal mode belonging to the imaginary frequency should describe the compression of one M···O bond concerted with the elongation of the other one (as for the I_a mechanism).

Within the present model, the above requirements cannot be met by third row transition elements with 7 or fewer 3d electrons, since they all have been shown to form heptacoordinated intermediates or transition states arising from the water exchange according to the A or I_a mechanism, but not the I_d one (Table 1). In all these cases, bond formation is more important than bond breaking. For this reason, the unsuccessful attempts to compute transition states for the I_d mechanism involved Ni^{II} and Zn^{II}, high-spin systems with 8 or 10 3d electrons that cannot form transition states for the A or I_a mechanism. All these calculations converged toward pentacoordinated species with two water molecules in the second coordination sphere. Obviously, hydrogen bonding is favored over the very weak M···O bonds. These calculations do, however, not exclude the existence of the I_d mechanism. They just indicate that within the present model, it is unlikely to exist.

In an improved model involving, for example, the second coordination sphere, the protons of the water molecules of the first sphere would be engaged in hydrogen bonding to solvent molecules of the second sphere. The two loosely bound water ligands, participating in the exchange reaction, would be deprived of the possibility of forming hydrogen bonds with water from the first coordination sphere. It remains to be checked whether they escape into the third coordination sphere and/or whether a transition state for the I_d mechanism with the appropriate imaginary mode exists.

The above discussion was based on Merbach's classification⁵ of reaction mechanisms, and substitutions proceeding via an experimentally undetectable and short-lived pentacoordinated intermediate were labeled (in this study) as D processes on the basis of their structures. In the Langford and Gray scheme,³ reactions involving experimentally inaccessible and, therefore, short-lived intermediates ($\tau \lesssim 100$ ps), fall into the I_a or I_d

classes. Water exchange of Mn^{II} and Fe^{III} would then proceed via the I_a mechanism, and some (or perhaps all) reactions, to which the D mechanism has been attributed (Table 4), might well follow the I_d one. Furthermore, it should be noted that the computed lifetimes (Table 3), ranging from 40 to 1100 ps, are only rough estimates, and most of them are comparable with the time for the rearrangement of the second coordination sphere. For this reason, a distinction of I_d and D mechanisms is not possible based on the present data.

Computational Details

All the calculations have been performed on Cray T3D, Cray Y-MP/M94, and HP 9000/735 computers with use of the GAMESS¹³ programs.

The basis sets of Stevens, Basch, Krauss, and Jasien¹⁴ were used for the transition metals, where the 1s, 2s, and 2p shells are represented by relativistic effective core potentials and the 3s, 3p, 4s, and 4p shells have double- ζ and the 3d triple- ζ quality. For O and H, 6-31G(d) basis sets¹⁵ were used ($a_{3d} = 1.20^{16}$).

All the ab initio calculations were first carried out at the restricted open shell Hartree–Fock level. Then, a singles–doubles CI involving the 3d orbitals and the entire virtual space was performed with C_1 symmetry for at least two states. If the coefficient of the HF wave function was <0.995 and/or the second state was of the same symmetry and close (<0.5 eV) to the first one, the final result was computed at the CAS-SCF level. This was necessary for most V^{III} and Co^{II} species. In cases where several electronic states exist, they all have been computed, but only the lowest state is reported. The transition states were located as described previously⁸ and their atomic coordinates are given in Table S2.

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Supporting Information Available: A listing of selected properties of reactants/products, transition states, and intermediates (Table S1) and the atomic coordinates of all transition states, including those of ref 8 (Table S2) (36 pages). See any current masthead page for ordering and Internet access instructions.

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