Hydration and Water Exchange of Zinc(II) Ions. Application of Density Functional Theory

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Abstract: Details of the hydration and water exchange mechanism of Zn^{2+} have been studied using density functional calculations with a variety of different basis sets. The computed structures and hydration energies for complexes of the type $[Zn(H_2O)_n]^{2+}$ with $n = 1-6$ are in good agreement with previous results obtained from *ab initio* calculations and self-consistent reaction field methods. Extension of our investigations to the second coordination (first solvation) sphere and thus to complexes of the general type $[Zn(H_2O)_n]^{2+} \cdot mH_2O$ with $n = 5$ and $m = 1, 2$ and $n = 6$ and $m = 1$ reveals two types of complexes having either one or two hydrogen bonds between first and second sphere water molecules. The water exchange mechanism of $[Zn(H_2O)_6]^{2+}$ is analyzed on the basis of the structures and energies of these complexes. Within the variations due to the different basis sets employed, the Zn−O bond length for water molecules in the first coordination sphere is between 2.0 and 2.1 Å, water molecules in the second coordination sphere between 3.6 and 4.1 Å and at the frontier of both spheres between 2.7 and 3.0 Å. Within the limitations of the present model, in which bulk water, counterions, and more than one exchanging water molecule have not been considered, a limiting dissociative (D) mechanism for the water exchange reaction on $[Zn(H_2O)_6]^{2+}$ is suggested. On the basis of the most reliable structures (i.e., those that could be verified with all levels of theory), the energy of activation for the water exchange is between 4.2 and 4.6 kcal/mol, depending on the basis set employed. A transition state for the interchange mechanism could not be localized. All optimizations invariably led to transition state structures that indicate a limiting D mechanism.

1. Introduction

The energetics and dynamics of the hydration of transition metal ions form the basis of many fundamental chemical and biochemical processes and have received the attention of many experimentalists in recent years. The application of *ab initio* molecular orbital calculations,[1−6] self-consistent reaction field methods,[7,8] and Monte Carlo simulations[9,10] to describe the hydration of transition metal ions has gained significant importance. In addition, considerable work has been done using molecular dynamics applied to the water exchange reactions of lanthanide ions.[11] The quality of these theoretical approaches has now developed to a level that allows one to comment on the mechanism of solvent exchange processes, even to the extent that such results mirror kinetic data.[6,11] In this respect, the application of density functional theory (DFT) to transition metal complexes should open new opportunities for studying the hydration of metal ions. This was recently shown by Ricca and Bauschlicher,[12] who computed the successive H_2O binding energies for $Fe(H_2O)_n^+$ with $n \leq 4$. In addition, Deeth and Elding[13] impressively modeled the exchange of H_2O in aqueous solution on $[Pd(H_2O)_4]^{2+}$, $[Pt(H_2O)_4]^{2+}$, and *trans*-$[PtCl_2(H_2O)_2]$ using a combination of DFT and molecular mechanics.

Our general interest in the mechanism of solvent exchange and ligand-substitution processes, coupled to the interpretation of volume of activation data,[14] has encouraged us to apply DFT to the description of the hydration and the water exchange processes of the Zn^{2+} ion. The reason for this is the limited kinetic data reported for the water exchange behavior of Zn^{2+} compared to other 3d metal ions, although the mechanistic details for this ion play an important role in the biological function of many metalloenzymes, such as carbonic anhydrase,

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carboxypeptidase A, thermolysin, and alcohol dehydrogenase. The former two enzymes are part of our previous studies,[15] and further insights to the fundamental reaction characteristics of Zn^{2+}, covered in the present work, will help in understanding the phenomena associated with the bioinorganic and solution chemistry of this metal ion.

We will first focus on the stepwise hydration of Zn^{2+} ions for coordination numbers between 1 and 6. In doing so, we follow recent *ab intio* studies presented by the groups of Glusker[4] and Kim,[5] who investigated aqua complexes of the general formula $[Zn(H_2O)_n]^{2+} \cdot mH_2O$, where $n \leq 4$ and m = 0, 1, 2, $n = 5$ and $m = 0$, 1 and $n = 6$ and $m = 0$. In the selected notation, "n" represents the number of water molecules in the first coordination sphere and "m" represents the number of water molecules in the second coordination (first solvation) sphere. Kim and co-workers[5] found that at 0 K, $[Zn(H_2O)_5]^{2+}$ and $[Zn(H_2O)_6]^{2+}$ are the most stable structures for Zn^{2+} ions surrounded by five and six water molecules, respectively. However, at room temperature, $[Zn(H_2O)_4]^{2+} \cdot H_2O$ is energetically as favorable as $[Zn(H_2O)_5]^{2+}$, whereas $[Zn(H_2O)_6]^{2+}$ is slightly more stable than $[Zn(H_2O)_5]^{2+} \cdot H_2O$ and $[Zn(H_2O)_4]^{2+} \cdot 2H_2O$. Glusker *et al.*[4] showed that total molecular energies of the gas-phase cluster $[Zn(H_2O)_6]^{2+}$, $[Zn(H_2O)_5]^{2+} \cdot H_2O$, and $[Zn(H_2O)_4]^{2+} \cdot 2H_2O$ differ by less than 0.4 kcal/mol and that a water molecule from the first coordination sphere can quite easily be lost to the second coordination sphere. Moreover, they found that it is not possible to optimize a minimum structure for $[Zn(H_2O)_7]^{2+}$, where seven water molecules are located in the first coordination sphere. Because this is in contrast to the assumption of a $[Zn(H_2O)_7]^{2+}$ complex made by Sandström and co-workers,[3] we further investigated the solvent environment of Zn^{2+} with seven water molecules, partitioned between the first and second coordination sphere, using DFT calculations.[16] Our calculations on gas-phase clusters also show that fully unconstrained optimizations with seven water molecules in the first coordination sphere of Zn^{2+} lead to structures with at least one water molecule in the second coordination sphere. This discrepancy has also been discussed by Rotzinger[6] who stated that *"Sandström's $[M(H_2O)_7]^{2+}$ species do not represent chemically relevant stationary points on the potential energy surface"*. Although consideration of thermodynamic and solvation effects might favor a heptaquazinc(II) complex over a hexaquazinc(II) complex with one loosely bound water molecule, which however seems unlikely from the evidence available, we extended our investigations to complexes of the general type $[Zn(H_2O)_n]^{2+} \cdot mH_2O$, where $n = 5$ and $m = 1$, 2 and $n = 6$ and $m = 1$. The results, reported in the second part of this paper, enable us to comment on the nature of this type of complexes and the basis set dependence of the results. Consideration of these structures as possible reactant and intermediate complexes for the water exchange reaction of hexaquazinc(II) enabled us to localize suitable transition states for this reaction.
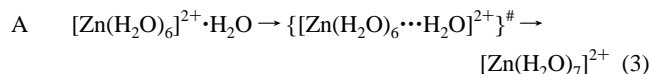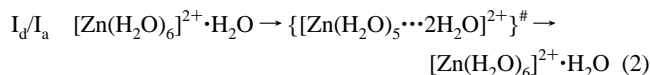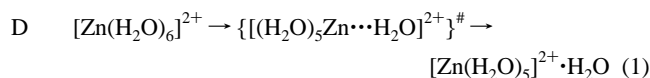
By comparing total energies and structural parameters of these gas-phase clusters, we can classify the substitution mechanism in terms of the nomenclature established by Langford and Gray.[17] This notation generally subdivides the substitution mechanism into associative (A), dissociative (D), and interchange (I) processes. While the A and D mechanisms have intermediates with coordination numbers increased or decreased

by 1, respectively, the I mechanism describes a concerted pathway with no detectable intermediate. Further differentiation of the latter process into I_a or I_d is used to denote substitution processes with some associative or dissociative activation, respectively. The attribution of the mechanism is based on the sign and the value of thermodynamic activation parameters like $\Delta V^{\#}$ and $\Delta S^{\#}$, the former being more diagnostic.[14] Negative values for these activation parameters show the trend toward an A mechanism, whereas positive values are an indication for a mechanism with D character. Swaddle showed that one can expect a maximum $\Delta V^{\#}$ of 13.6 cm^3/mol for the limiting dissociative water exchange (D mechanism) of hexaquazinc(II).[18] In order to find an intrinsic measure that correlates with this activation parameter, we summarize all Zn—O bond lengths of the transition state structure and the reactant complex, respectively. The difference between these values will lead to changes in bond length that parallel the sign and value of the volume of activation. Rotzinger has shown that this procedure produces reasonable values for the water exchange reaction on Ni^{2+}, V^{2+}, and Ti^{3+}.[6]

2. Methods

(a) Models. The models used in the present work are based on the gas-phase and thus cannot be transferred rigorously to solution. Bulk water, counterions, and more than one water molecule in the second coordination (first solvation) sphere have been neglected (see further discussion in Sections 3 and 4, respectively).

A crucial aspect of the water exchange reaction is to simulate the interchange nature of the substitution process during which a water molecule in the first coordination sphere is exchanged with a water molecule in the second coordination sphere. Therefore, we first studied the hydration of Zn^{2+} ions, considering up to seven water molecules, thus including the limiting dissociative and associative substitution modes of the octahedral hexaqua cation. In order to determine the most favorable mechanism for this symmetrical exchange reaction, we analyzed all possible mechanisms. For Zn^{2+} we first investigated the limiting dissociative process in eq 1 that forms a five-coordinated intermediate complex of the type $[Zn(H_2O)_5]^{2+} \cdot H_2O$, with one water molecule located in the second coordination sphere. Next we consid-

$$D \quad [Zn(H_2O)_6]^{2+} \rightarrow \{[(H_2O)_5Zn \cdots H_2O]^{2+}\}^{\#} \rightarrow$$
$$[Zn(H_2O)_5]^{2+} \cdot H_2O \quad (1)$$

$$I_d/I_a \quad [Zn(H_2O)_6]^{2+} \cdot H_2O \rightarrow \{[Zn(H_2O)_5 \cdots 2H_2O]^{2+}\}^{\#} \rightarrow$$
$$[Zn(H_2O)_6]^{2+} \cdot H_2O \quad (2)$$

$$A \quad [Zn(H_2O)_6]^{2+} \cdot H_2O \rightarrow \{[Zn(H_2O)_6 \cdots H_2O]^{2+}\}^{\#} \rightarrow$$
$$[Zn(H_2O)_7]^{2+} \quad (3)$$

ered an associatively/dissociatively activated interchange mechanism (eq 2) that, from an experimental point of view, has no detectable intermediate. If, however, theoretically a complex of the type $[Zn(H_2O)_5]^{2+} \cdot 2H_2O$ that corresponds to a local minimum could be localized, the energy difference to the transition state complex should be extremely small, otherwise this structure would resemble a true intermediate, which itself is an indication of a limiting dissociative mechanism. Because of our inability to localize chemically relevant stationary structures for $[Zn(H_2O)_7]^{2+}$ or transition state structures for $\{[Zn(H_2O)_6 \cdots H_2O]^{2+}\}^{\#}$, no further calculations concerning a limiting associative mechanism (eq 3) were performed, and the operation of such a mechanism in the water exchange on Zn^{2+} was therefore ruled out.

In order to trace the change in bond length occurring on reaching the transition state structure and thus to find a measure that parallels the volume of activation, we hence summarized all the Zn—O bond lengths in the reactant and in the transition state complex, respectively.

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Table 1. Selected Structural Parameters[a] and Point Group (PG) Assignment for the Complexes $[Zn(H_2O)_n]^{2+}$ with $n = 1-6$

	SHA1	6-311G	6-311G(d)	6-311+G(d)	6-311+G(d,p)	PG
$[Zn(H_2O)]^{2+}$	1.887	1.877	1.878	1.879	1.883	C_{2v}
$[Zn(H_2O)_2]^{2+}$	1.878	1.857	1.858	1.872	1.876	D_{2d}
$[Zn(H_2O)_3]^{2+}$	1.948	1.918	1.923	1.941	1.947	D_3
$[Zn(H_2O)_4]^{2+}$	2.000	1.971	1.977	1.997	2.004	S_4
$[Zn(H_2O)_5]^{2+}$	2.114, 2.114, 2.046, 2.031, 2.031 (2.067)[b]	2.076, 2.076, 2.027, 2.010, 2.010, (2.040)[b]	2.082, 2.082, 2.032, 2.016, 2.016, (2.046)[b]	2.119, 2.119, 2.045, 2.028, 2.028, (2.068)[b]	2.127, 2.127, 2.053, 2.038, 2.038, (2.077)[b]	C_{2v}
$[Zn(H_2O)_6]^{2+}$	2.114	2.091	2.095	2.119	2.130	T_h

[a] Because of our main interest in this work, only the $r(Zn-O)$ values [Å] are reported. For further details concerning the geometries of the calculated complexes, please consult the Supporting Information. [b] Mean values of the bond lengths used in Figure 2 are given in parentheses.

According to eq 4, the difference of these values leads to the structural change associated with the activation process during water exchange. The comparison of such values with available experimental volumes of activation clearly shows their reliability and applicability.[6]

$$\Delta = \sum_{i=1}^{n}\{r(Zn-O_i)\}^{\#} - \sum_{i=1}^{n}r(Zn-O_i) \qquad n = 6 \text{ for eq 1} \qquad (4)$$

$$n = 7 \text{ for eq 2}$$

The assignment of the intimate mechanism was then possible from a comparison of the energies of activation for eqs 1 and 2. In addition, bond distances between zinc and oxygen of water molecules in the second coordination sphere were also used for the mechanistic assignment. Due to the lack of an experimental volume of activation for water exchange on Zn^{2+}, structural changes expressed by means of the Δ value were compared with calculated or measured values for other elements reported in the literature.[14]

(b) Computational Details. All calculations used Gaussian 94[19] with the B3LYP[20,21] three-parameter hybrid density functional. The basis sets used were 6-311G and 6-311G(d),[22] 6-311+G(d) and 6-311+G(d,p),[23] and the optimized Schaefer−Horn−Ahlrichs split valence basis[24] set augmented with p- and d-type polarization functions (SHA1). Transition state optimizations used the synchronous transient-guided quasi-Newton search algorithms.[25] These techniques and results obtained with additional basis set modifications are explained in detail in the Supporting Information.

3. Results and Discussion

Basis Set Dependency. In general, the results of the calculations depend quite strongly on the basis set used. We have found, however, that the SHA1 basis set gives geometries very close to those found with 6-311+G(d,p); 6-311G(d), however, is the only basis for which we were able to locate suitable transition states for the water exchange reaction of Zn^{2+} surrounded by seven water molecules. The basis set depend-

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Table 2. Hydration Energies [kcal/mol] for the Reaction $Zn^{2+} + nH_2O \rightarrow [Zn(H_2O)_n]^{2+}$

n	SHA1	6-311G	6-311G(d)	6-311+g(d)	6-311+G(d,p)
1	−106.3	−110.8	−104.5	−105.4	−101.5
2	−199.6	−213.2	−200.6	−195.8	−188.1
3	−262.9	−277.3	−259.9	−254.0	−243.0
4	−312.9	−329.6	−308.6	−299.0	−285.1
5	−344.6	−366.9	−343.7	−326.7	−309.6
6	−373.4	−400.5	−375.6	−351.9	−332.4

[a] For total energies and zero-point energies [au], refer to the Supporting Information (Table 2_sup).

encies are discussed in detail in the Supporting Information. Unless otherwise noted, all geometries given in the text are those found at the highest level of theory (i.e., with 6-311+G(d,p)).

(a) $[Zn(H_2O)_n]^{2+}$ with $n = 1-6$. We first consider hydrated zinc ions of the general type $[Zn(H_2O)_n]^{2+}$, where $n = 1-6$. Thus, all water molecules are located only in the first coordination sphere. Selected structural parameters and hydration energies of the complexes under consideration are summarized in Tables 1 and 2, respectively. Schematic presentations of the final molecular geometries obtained are shown in Figure 1. There have been several previous investigations dealing with the hydration of divalent zinc ion using *ab initio* calculations[1-5] and statistical simulations.[7-10] However, to our knowledge this is the first study dealing with the results obtained using density functional calculations in combination with a series of different basis sets.

The structure obtained for the monoaqua complex has C_{2v} symmetry and a Zn−O bond length of 1.883 Å. In Figure 2 the calculated Zn−O bond lengths are plotted as a function of the number of ligands n located in the first coordination sphere. We find a lengthening of the Zn−O bond as n increases except for a slight shortening on going from $[Zn(H_2O)]^{2+}$ to $[Zn(H_2O)_2]^{2+}$. This, however, can be attributed to the formation of a hybrid orbital from an unfilled s and a filled d_{z^2} orbital. The resulting lobes pointing to opposite sides of the metal ion lead to the preferred linear structure of the diaqua cation with H_2O ligands staggered against each other. The overall structure of this complex has D_{2d} symmetry. The structure for $[Zn(H_2O)_3]^{2+}$, found to be a local minimum with respect to its potential energy surface, has D_3 symmetry and a Zn−O bond length of 1.947 Å. The structure of $[Zn(H_2O)_4]^{2+}$ belongs to the S_4 point group and has a Zn−O bond length of 2.004 Å. For the pentaqua complex, which has C_{2v} symmetry, three different Zn−O bond lengths were obtained, thus yielding a mean value of 2.077 Å. The octahedral hexaqua complex has T_h symmetry and a Zn−O bond length of 2.130 Å. The Zn−O distances in this complex obtained from other computational studies[1-10] vary between 1.90 and 2.14 Å. Among these, Marcos *et al.*[7] found that their gas-phase value of 2.05 Å is increased to 2.07 Å when the hexaqua cation is embedded in a solvent reaction field, while the Zn−O distance measured in
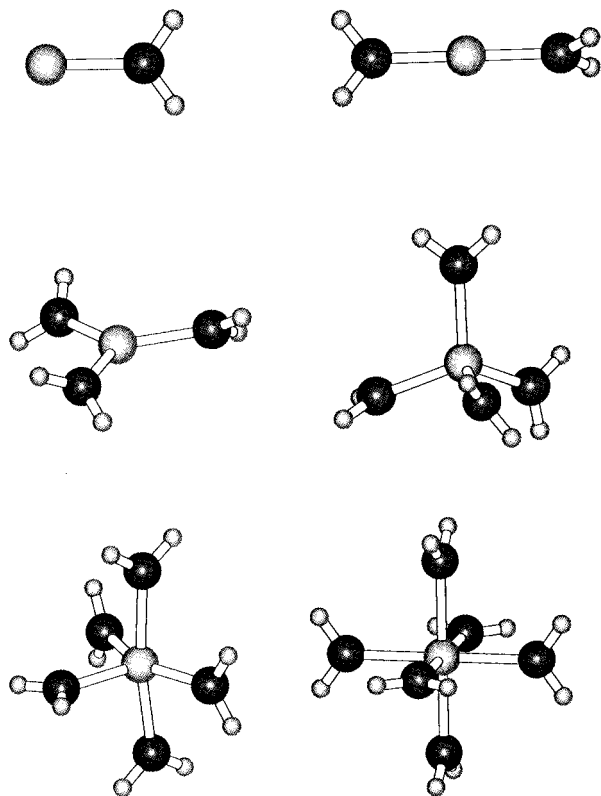
Figure 1. Molecular geometries of $[Zn(H_2O)_n]^{2+}$ with $n = 1-6$ from DFT (B3LYP) calculations of the complexes using various basis sets. Selected structural parameters, hydration energies and point group assignment are listed in Tables 1 and 2, respectively.
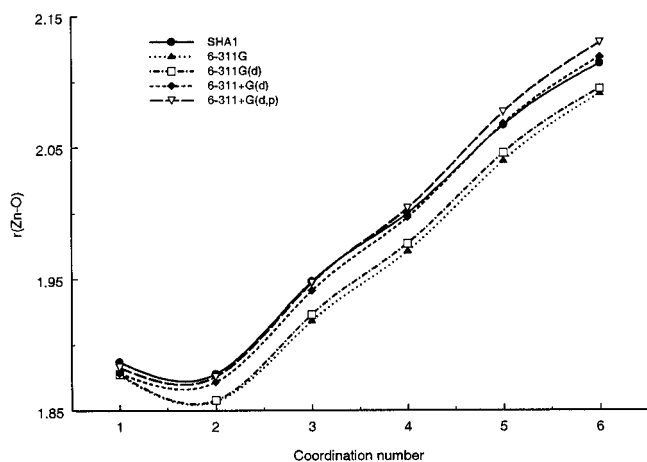

Figure 2. The zinc−oxygen bond length $r(Zn-O)$ [Å] as a function of coordination number n. All results were obtained using the B3LYP functional in conjunction with the basis set shown in the legend above.

aqueous solution is 2.08−2.10 Å.[26] This implies that the gas-phase geometries are almost independent of solvent effects. Therefore, the comparison of calculated *in vacuo* Zn−O distances with observed Zn−O bond lengths in aqueous solution is justified. As a whole, the calculated data presented for $r(Zn-O)$ are in reasonable agreement with the corresponding experimental and calculated ones.

Gas-phase hydration energies for eq 5, based on the hydration energies given in Table 2, are plotted as a function of the coordination number n in Figure 3. The negative values of these energies equal the binding energies between the cation and water
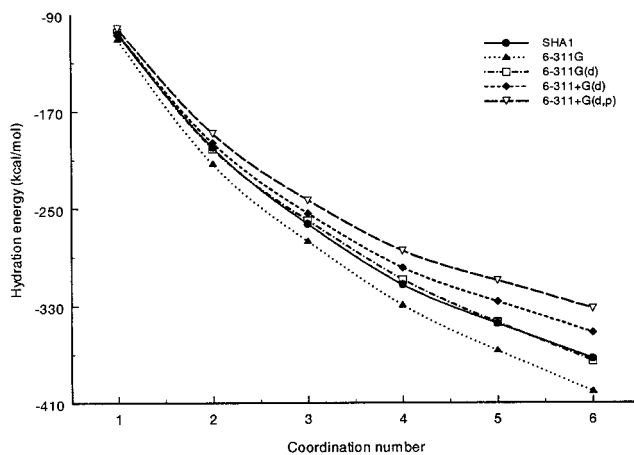
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Figure 3. Hydration energy as a function of the coordination number n for $Zn^{2+} + nH_2O \rightarrow [Zn(H_2O)_n]^{2+}$. All results were obtained using the B3LYP functional and the basis sets shown in the legend above.

and division of these values by the coordination number n yields the binding energy per water molecule of the complexes $[Zn(H_2O)_n]^{2+}$.

$$Zn^{2+} + nH_2O \rightarrow [Zn(H_2O)_n]^{2+} \qquad (5)$$
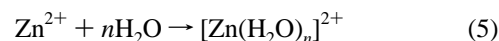
The plot in Figure 3 shows that, as the coordination number increases, the hydration becomes less exothermic and, thus, the binding energy per water molecule becomes smaller. This behavior can be attributed to an increasing ligand−ligand repulsion when the first coordination sphere is subsequently filled with water molecules. The hydration energy for the monoaquazinc(II) complex varies with respect to the basis set applied between −106.3 and −101.5 kcal/mol. The total gas-phase hydration energy for the hexaquazinc(II) complex at the different levels of theory applied lies between −400.5 and −332.4 kcal/mol. These results are in good agreement with the findings of other groups.[1,4,5,7,9] Note, however, that the calculated gas-phase energies do not consider thermal or entropic corrections and, therefore, cannot be compared with estimations for the hydration energy of Zn^{2+} based on reaction field simulations[7−10] or experimental studies.[27] Consideration of a second coordination sphere (i.e., 12 water molecules at a Zn−O distance of approximatetly 4 Å)[9] and further corrections due to the thermodynamics of the system in solution should, in principle, refine the hydration energy obtained for the hexaquazinc(II) complex. However, consideration of the complete second coordination sphere by means of a supermolecular approach, where all 12 water molecules in the second coordination sphere are treated explicitly, is prevented by the complexity of the system.

(b) $[Zn(H_2O)_n]^{2+} \cdot mH_2O$ with $n = 5$ and $m = 1$, 2 and $n = 6$ and $m = 1$. In this section, complexes of the general type $[Zn(H_2O)_n]^{2+} \cdot mH_2O$ are presented by means of their coordination numbers in the first (n) and second (m) coordination sphere. The extension of our studies to complexes with water molecules located in the second coordination sphere generally revealed two types of conformers, which have either one or two hydrogen bonds between water molecules in the first and second coordination sphere. The former type is abbreviated as $\{n,m\}$ and the latter as (n,m). If the structure presented belongs to a first-order saddle point with respect to the potential energy surface, it is marked with a superscript pound sign (#). Selected structural parameters and relative energies of all of the

(27) Burgess, J. *Ions in Solution: Basic Principles of Chemical Interactions;* Ellis Horwood Ltd.: Chichester, England, 1988; p 55.

Table 3. Selected Structural Parameters[a] and Point Group Assignment for the Complexes $[Zn(H_2O)_n]^{2+} \cdot m H_2O$ with $n = 5$ and $m = 1, 2$ and $n = 6$ and $m = 1$

		SHA1		6-311G(d)		6-311+G(d,p)		
$n + m$[b]	(n,m)	$r(Zn-O)_{II}$	$r(Zn-O)_I$	$r(Zn-O)_{II}$	$r(Zn-O)_I$	$r(Zn-O)_{II}$	$r(Zn-O)_I$	PG
6	$(5,1)^{\#}$	2.689	2.104, 2.104, 2.050, 2.055, 2.055	2.898	2.020, 2.020, 2.080, 2.080, 2.023	2.829	2.051, 2.051, 2.118, 2.118, 2.055	C_{2v}
6	$(5,1)$	3.594	2.037, 2.037, 2.119, 2.119, 2.028	3.654	2.027, 2.027, 2.083, 2.083, 2.009	3.675	2.041, 2.041, 2.133, 2.133, 2.035	C_2
6	$\{5,1\}^{\#}$			3.061	2.052, 2.052, 2.005, 2.072, 2.043			C_S
6	$\{5,1\}$	3.984	2.113, 2.113, 1.991, 2.075, 2.038	4.102	2.038, 2.038, 2.087, 2.097, 2.043	4.104	2.106, 2.106, 2.010, 2.100, 2.049	C_S
7	$(6,1)$	3.850	2.103, 2.103, 2.121, 2.121, 2.148, 2.148	3.851	2.078, 2.078, 2.087, 2.087, 2.113, 2.113	3.932	2.110, 2.110, 2.134, 2.134, 2.158, 2.158	C_2
7	$(5,2)$	3.809, 3.809	2.026, 2.026, 2.052, 2.089, 2.089	3.814, 3.814	2.010, 2.010, 2.040, 2.065, 2.065	3.876, 3.876	2.032, 2.032, 2.061, 2.105, 2.105	C_2
7	$\{6,1\}$	3.956	2.137, 2.052, 2.113, 2.122, 2.130, 2.130	4.150	2.104, 2.035, 2.110, 2.097, 2.106, 2.106	4.236	2.138, 2.055, 2.148, 2.138, 2.143, 2.143	C_S
7	$\{5,2\}^{\#}$			4.197, 3.026	2.063, 2.007, 2.012, 2.066, 2.066			C_S
7	$\{5,2\}$	4.070, 4.070	2.046, 2.137, 2.137, 2.002, 2.002	4.132, 4.132	2.056, 2.061, 2.061, 2.007, 2.007	4.148, 4.148	2.056, 2.148, 2.148, 2.009, 2.009	C_{2v}

[a] Bond lengths are given in [Å]; $r(Zn-O)_{II}$ refers to the distance of the water molecule in the second coordination sphere; $r(Zn-O)_I$ refers to that of the water molecules in the first coordination sphere. [b] n represents the number of water molecules in the first coordination sphere, m represents the number of water molecules in the second coordination (first solvation) sphere.
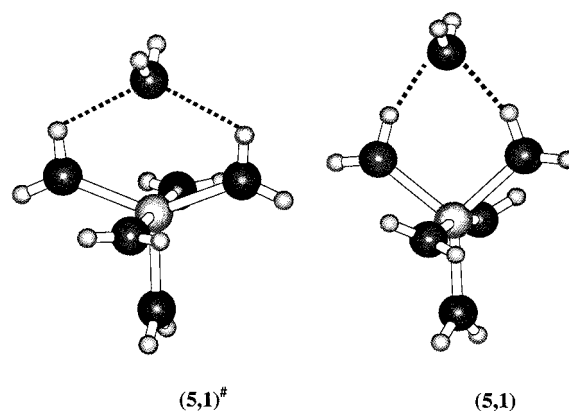
Table 4. Relative Energies[a] [kcal/mol] for the Reactions $[Zn(H_2O)_n]^{2+} \cdot m H_2O \rightarrow [Zn(H_2O)_{n'}]^{2+} \cdot m' H_2O$ with $n, n' \geq 5$ and $m, m' = 1, 2$ and $n, n' = 6$ and $m, m' = 1$

$n + m$	$(n,m) \rightarrow (n',m')$	SHA1	6-311G(d)	6-311+G(d,p)
6	$(6,0) \rightarrow (5,1)^{\#}$	4.6	7.4	4.2
6	$(5,1)^{\#} \rightarrow (5,1)$	−4.2	−2.9	−3.2
6	$(6,0) \rightarrow \{5,1\}^{\#}$		7.8	
6	$\{5,1\}^{\#} \rightarrow \{5,1\}$		−2.8	
7	$\{6,1\} \rightarrow \{5,2\}^{\#}$		6.8	
7	$\{5,2\} \rightarrow \{5,2\}^{\#}$		−3.3	
7	$(6,1) \rightarrow (5,2)$	−7.4	−2.5	−5.5

[a] Energies given in the table equal the difference of the total energies including zero-point energies of each of the complexes. See the Supporting Information (Table 4_sup) for total energy and zero-point energy values [au].

complexes obtained are summarized in Tables 3 and 4, respectively. In order to distinguish between $Zn-O$ bond lengths between first and second sphere water molecules, these bond distances are written as $r(Zn-O)_I$ and $r(Zn-O)_{II}$, respectively. Despite the variations due to the different basis sets employed, the $r(Zn-O)_I$ values of water molecules in the first coordination sphere are between 2.0 and 2.1 Å, whereas the bond lengths $r(Zn-O)_{II}$ belonging to water molecules of the second sphere are at least greater than 3.6 Å. However, the latter exhibit a significant basis set dependence, and distances up to 4.1 Å are reached. In the transition states, where water is almost at the frontier of the two spheres, the $r(Zn-O)_{II}$ bond length is between 2.7 and 3.0 Å. These values fit reasonably well with the bond lengths obtained from both simulation[9,10] and experiment.[28]

Complexes $(5,1)^{\#}$ and $(5,1)$ are shown in Figure 4. The former complex represents a possible transition state formed in the water exchange reaction according to a limiting dissociative mechanism (eq 1), whereas the latter belongs to the corresponding intermediate. Selected structural parameters and point group assignments are summarized in Table 3. The structure of complex $(5,1)^{\#}$ could be localized using all basis sets under consideration. Frequency analyses revealed one imaginary mode, which shows the movement of the water molecule to

(28) (a) Dagnall, S. P.; Hague, D. N.; Towl, A. D. C. *J. Chem. Soc., Farady Trans. 2* **1982**, *78*, 2161. (b) Licheri, G.; Paschina, G.; Piccalagua, G.; Pinna, G. *Z. Naturforsch. A: Phys. Sci.* **1982**, *37*, 1205.

(5,1)$^{\#}$ **(5,1)**

Figure 4. Transition state complex $(5,1)^{\#}$ and intermediate complex $(5,1)$ obtained using the B3LYP functional and the basis sets given in Tables 3 and 4, respectively.

the metal center. The bond length from the metal center to the oxygen atom of the leaving water molecule $r(Zn-O)_{II}$ is 2.829 Å. Consideration of $[Zn(H_2O)_6]^{2+}$ (see Figure 1 and Table 1) as the reactant complex shows that lengthening of the $Zn-O$ distance on reaching the transition state structure occurs along the two-fold axis. According to eq 4, further information concerning the mechanistic details is gained using the sums of the $Zn-O$ bond lengths of the reactant $[Zn(H_2O)_6]^{2+}$ and the transition state complex, respectively. The difference between the resulting $\sum_i r(Zn-O)_i$ values, which are summarized in Table 5, yields a Δ value, which indicates whether the structure of the reactant complex is expanded or compressed on reaching the transition state and thus parallels the volume of activation.[6] On the highest level of theory, this value is 0.442 Å. The positive sign of this value implies an expansion of the reactant structure toward the transition state structure and therefore verifies the dissociative character of the mechanism. After the transiton state is passed, intermediate $(5,1)$, which has C_2 symmetry, is formed. At this stage, the $r(Zn-O)_{II}$ value is 3.675 Å. The relative stability of this intermediate compared to the transition state structure is −3.2 kcal/mol (Table 4). This, however, implies that the intermediate truly resembles a detectable conformer. Moreover, due to the fact that the effect of a seventh water molecule has not been discussed up until to

Table 5. $\sum_i r(\text{Zn}-\text{O})_i$ [Å] and Δ Values [Å] According to Eq 4 for Intermediate and Transition State Structures in Reactions 1 and 2

	SHA1	6-311G(d)	6-311+G(d,p)
$(6,0) \rightarrow (5,1)^{\#}$			
$\sum_i\{r(\text{Zn}-\text{O})_i\}^{\#\ a}$	13.052	13.121	13.222
$\sum_i r(\text{Zn}-\text{O})_i{}^{\,b}$	12.684	12.570	12.780
Δ^c	0.368	0.551	0.442
$(6,0) \rightarrow \{5,1\}^{\#}$			
$\sum_i\{r(\text{Zn}-\text{O})_i\}^{\#\ a}$		13.285	
$\sum_i r(\text{Zn}-\text{O})_i{}^{\,b}$	12.684	12.570	12.780
Δ^c		0.715	
$\{6,1\} \rightarrow \{5,2\}^{\#}$			
$\sum_i\{r(\text{Zn}-\text{O})_i\}^{\#\ a}$		17.437	
$\sum_i r(\text{Zn}-\text{O})_i{}^{\,d}$	16.630	16.708	17.001
Δ^c		0.729	

^{a} Sum of all Zn−O bond lengths in the transition state structure. ^{b} Sum of all Zn−O bond lengths in the (6,0) complexes summarized in Table 1. ^{c} Δ value according to eq 4. ^{d} Sum of all Zn−O bond lengths for the {6,1} complexes summarized in Table 3.

$\{5,1\}^{\#}$ $\{5,1\}$
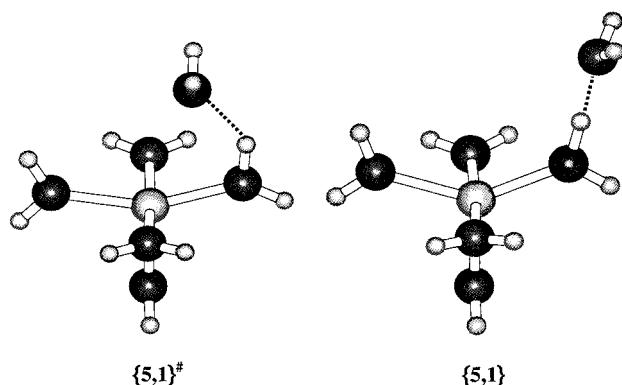
Figure 5. Transition state complex $\{5,1\}^{\#}$ and intermediate complex $\{5,1\}$ obtained using B3LYP/6-311G(d)//B3LYP/6-311G(d).

now, the calculated Δ values resemble a limiting dissociative mechanism. Consideration of the applicability of each of the basis sets to reproduce hydration energies discussed (see the discussion in the Supporting Information) implies that the energy of activation obtained using the SHA1 and 6-311+G(d,p) basis sets are the most reasonable ones. The activation energies, which are summarized in Table 4, thus obtained are 4.6 and 4.2 kcal/mol, respectively.

Further studies on possible transition states and intermediates formed from reactant $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$, which resemble the complexes implied by eq 1 and thus a limiting dissociative mechanism, are depicted in Figure 5. Complexes $\{5,1\}^{\#}$ and $\{5,1\}$, both belonging to the C_S point group, represent an additional transition state and intermediate, respectively. The $r(\text{Zn}-\text{O})_{\text{II}}$ bond length of the former conformer calculated at the 6-311G(d) level of theory is 3.061 Å and is expanded on reaching the intermediate to 4.102 Å. The leaving water molecule now is only bound to one water molecule of the first coordination sphere and thus exhibits only one hydrogen bond. Consequently, the pathway for the leaving ligand lies rather in the mirror plane bisecting the structure of the complex than along a two-fold axis. Interestingly, these complexes resemble the structures for the water exchange on Ni^{2+} recently suggested by Rotzinger.[6]

Although the structure of the intermediate $\{5,1\}$ was obtained using all of the basis sets shown in Tables 3 and 4, optimizations for the transition state structure $\{5,1\}^{\#}$ were only successful with the 6-311G(d) basis set. The application of the higher triple-ζ basis set, 6-311G+(d,p), surprisingly yields transition state $(5,1)^{\#}$ rather than $\{5,1\}^{\#}$. Moreover, when the SHA1 basis set was

used for optimization and frequency analysis of the intermediate, one imaginary vibrational frequency and thus a first-order transition state is predicted instead of a local minimum. This, however, clearly demonstrates a significant basis set dependence of the structures under consideration and requires the application of a series of different basis sets. The fact that the less-sophisticated basis set yields stable points with respect to the potential energy surface implies that structures $\{5,1\}^{\#}$ and $\{5,1\}$ might be artifacts and complexes $(5,1)^{\#}$ and $(5,1)$ are better to describe the transition state and the intermediate of eq 1.

Consideration of the total energies (see Supporting Information) allows us to derive the relative stabilties of $\{5,1\}^{\#}$ and $\{5,1\}$ compared to their corresponding complexes $(5,1)^{\#}$ and $(5,1)$. In general, independent of the basis set used, the latter pair of complexes is more stable, although the energy difference for the $\{5,1\}$ and $(5,1)$ complexes is surprisingly small. For the transition states $\{5,1\}^{\#}$ and $(5,1)^{\#}$, the same behavior can be observed, and the energy difference that favors the latter is 0.5 kcal/mol. The energy of activation for eq 1 using complex $\{5,1\}^{\#}$ as the transition state was calculated to be 7.8 kcal/mol (Table 4). This value almost equals the one obtained for the $(5,1)^{\#}$ transition state with the same basis set. The Δ value according to eq 4 was calculated to be 0.715 Å (Table 5) and thus also verifies that the complexes presented belong to a dissociative mechanism. However, due to the limitations concerning the verification of the conformers $\{5,1\}^{\#}$ and $\{5,1\}$ with the other basis sets used, complexes $(5,1)^{\#}$ and $(5,1)$ seem to be more suitable for describing the transition state and intermediate of the limiting dissociative water exchange mechanism (eq 1) of Zn^{2+}.

For further analysis of the dissociative pathway, eq 2 was studied in order to verify whether a dissociatively activated interchange mechanism (I_d) is appropriate for the water exchange reaction on Zn^{2+}. The structures optimized for the reactant $\{6,1\}$, transition state $\{5,2\}^{\#}$, and intermediate $\{5,2\}$ are shown in Figure 6. Despite the seventh water molecule, the transition state and the intermediate look quite similar to the conformers $\{5,1\}^{\#}$ and $\{5,1\}$. In addition, the same problems concerning the basis set dependence discussed above were encountered for the $\{5,2\}^{\#}$ complex. Therefore, transition state $\{5,2\}^{\#}$ could not be verified using either the SHA1 or 6-311+G(d,p) basis sets. Consequently, only the 6-311G(d) basis set leads to the transition state shown in Figure 6. Although the structures of the reactant and intermediate could be optimized successfully using the other basis sets under consideration, further comparisons with the complexes employed for the D mechanism (eq 1) are limited to the results obtained with the 6-311G(d) basis set. A more detailed description of the results obtained using the SHA1 and 6-311+G(d,p) basis sets is given in the Supporting Information.

The seventh water molecule of conformer $\{6,1\}$, which has C_S symmetry, is located in the second coordination sphere and shows one hydrogen bond to a water molecule in the first coordination sphere. The distance from the metal center was calculated to be 4.150 Å. Surprisingly, on reaching the transition state structure $\{5,2\}^{\#}$, which also has C_S symmetry, this water molecule still remains in the second coordination sphere at a distance of 4.197 Å from the metal and shows no tendency to penetrate the first coordination sphere. The leaving water ligand, however, is now at a distance of 3.026 Å from the metal center. After the transition state is passed, the intermediate $\{5,2\}$ is reached and both water molecules are held in the second coordination sphere by one hydrogen bond each. The bond length $r(\text{Zn}-\text{O})_{\text{II}}$ of both water molecules was calculated to be 4.132 Å, thus resulting in a structure with C_{2v}
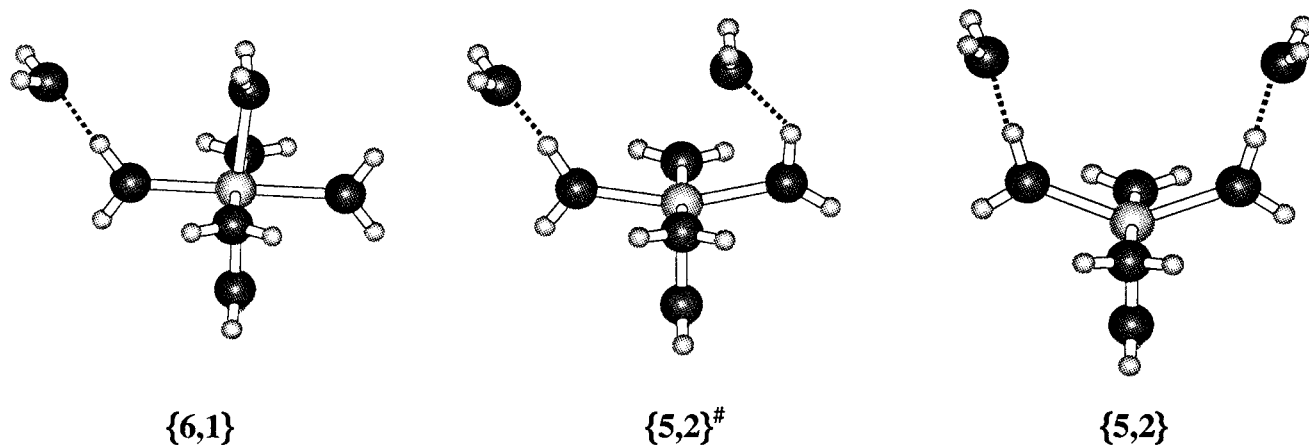
Figure 6. Reactant {6,1}, transition state {5,2}$^{\#}$, and intermediate complex {5,2} obtained using B3LYP/6-311G(d)//B3LYP/6-311G(d).
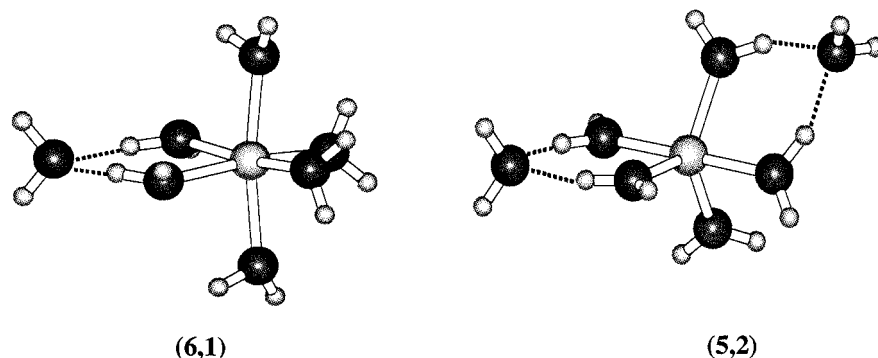

Figure 7. Complexes (6,1) and (5,2) that do not fit into a reaction scheme but are local minima with respect to their potential energy surface. The structures were obtained using the B3LYP functional an the basis sets given in Tables 3 and 4, respectively.

symmetry. The energy of activation for the transformation of {6,1} into {5,2}$^{\#}$ is 6.8 kcal/mol, and the Δ value is 0.729 Å. Although this energy of activation is 1.0 kcal/mol smaller than the correponding energy for the conformer {5,1}$^{\#}$ in eq 1, structural parameters such as the Zn–O bond length, the Δ value, and relative stabilities between the transition state and the intermediate indicate that complex {5,2}$^{\#}$ does not resemble the transition state structure of an I_d mechanism. Such a structure should have the seventh water molecule closer to the metal center than in the reactant complex, which is not the case for the transition state structure {5,2}$^{\#}$. This is also reflected by the Δ value, which is slightly higher than the one calculated using the 6-311G(d) basis set for the limiting D mechanism (eq 1). Furthermore, the relative stability of intermediate {5,2} compared to that of {5,2}$^{\#}$ shows that the former conformer is more stable than the latter by −3.3 kcal/mol. Therefore, after {5,2}$^{\#}$ is passed, the reaction yields an intermediate that is as stable as the ones found for the limiting dissociative mechanism, thus ruling out any dissociatively activated interchange character in this model. As a whole, structures {5,2}$^{\#}$ and {5,2} can be considered as hydrated transition state {5,1}$^{\#}$ and intermediate {5,1}, respectively. Therefore, suitable transition state and intermediate complexes for an I_d mechanism where the entering/ leaving water molecule exhibits one hydrogen bond toward a water molecule in the first coordination sphere could not be localized, and such a mechanism can be ruled out within the framework of this approach.

Further studies on the I_d mechanism (eq 2) revealed two more types of complexes. In contrast to the structures discussed above, the water molecule in the second coordination sphere now exhibits two hydrogen bonds toward water molecules in the first coordination sphere. Complexes (6,1) and (5,2), which are both local minima with respect to their potential energy surface, are presented in Figure 7. The localization of a suitable transition state structure that connects the reactant (6,1) with the intermedate (5,2) was not possible, and thus, no pathway for the transformation of (6,1) into (5,2) was found. This is either due to the fact that these two conformers are not part of the exchange mechanism at all or that no water exchange mechanism using conformers with seven water molecules is possible for Zn^{2+}. It follows that the operation of a mechanism with a dissociatively activated interchange character (I_d) for water exchange on Zn^{2+} is unlikely within this model. Note, however, that this may depend on the approximations employed in our studies. The situation may change when more water molecules are added to the second coordination (first solvation) sphere and solvent-assisted reactions could in principle occur.

Structural data and relative energies of complexes (6,1) and (5,2), which both have C_2 symmetry, are reported in Tables 3 and 4, respectively. The bond length $r(\text{Zn–O})_{\text{II}}$ of the former conformer is 3.932 Å. The latter complex shows only slight deviations from these bond distances, and the $r(\text{Zn–O})_{\text{II}}$ value is 3.876 Å. In general, from consideration of the relative energies obtained on the highest level of theory, it follows that conformer (5,2) is more stable than (6,1) by −5.5 kcal/mol (Table 4). Thus, conformer (5,2) is too stable to act as a possible intermediate produced from complex (6,1). This statement is also supported by consideration of the water−water interaction energy.[29] On our highest level of theory, the water dimer binding energy was calculated to be −3.5 kcal/mol (see the Supporting Information) thus showing that even if the dimerization of water from complex (6,1) is considered, formation of conformer (5,2) is still more favorable.

(29) We gratefully acknowledge the suggestion made by one of the reviewers of this manuscript.

4. Conclusions

The results presented in the first part of section 3 show that the application of density functional theory in conjunction with adequate basis sets produces reasonable structures for aqua complexes of the general type $[Zn(H_2O)_n]^{2+}$ with $n = 1-6$. The general trend that the Zn−O bond length increases with increasing coordination number including the exception for the diaqua complex could be reproduced. The structural parameters obtained for these complexes are in good agreement with those found in the literature. With respect to the Zn−O bond lengths, the values obtained with the SHA1 and the 6-311+G(d,p) basis sets resemble each other closely. As a whole, energetic and structural results obtained using the B3LYP functional and the 6-311+G(d,p) basis set are most reasonable for this type of complexes.

Extension of our studies on aqua complexes of Zn^{2+} to complexes with water molecules in the second coordination sphere generally revealed two types of complexes showing either one or two hydrogen bonds between water molecules in the first and second coordination spheres. On the basis of the structures obtained with the basis sets under consideration, the water environment of Zn^{2+} can be separated into three regions. First, the water molecules in the first coordination sphere, which have Zn−O bond lengths between 2.0 and 2.1 Å. This distance is increased to 3.6−4.1 Å for water molecules in the second coordination sphere. At the frontier of both spheres, this bond length lies between 2.7 and 3.0 Å. The water exchange reaction was simulated using the complexes discussed so far. For the limiting dissociative mechanism (eq 1), $[Zn(H_2O)_6]^{2+}$ was used as reactant. When one Zn−O bond length was expanded, we could localize two transition states having either one or two hydrogen bonds to the leaving water molecule (see complexes $(5,1)^{\#}$ and $\{5,1\}^{\#}$ in Figures 4 and 5, respectively). Consequently, in complex $(5,1)^{\#}$ the path of the leaving water is along the two-fold axis, whereas it lies in the mirror plane for complex $\{5,1\}^{\#}$. It is, however, noteworthy that the latter complex could only be optimized with the 6-311G(d) basis set. Verifications using other, larger basis sets were not possible. Optimizations for the desired complex either resulted in the $(5,1)^{\#}$ structure or did not converge at all. Therefore, complexes $(5,1)^{\#}$ and, thus, $(5,1)$ (Figure 4) are more likely to resemble the transition state and intermediate of a limiting D mechanism than complexes $\{5,1\}^{\#}$ and $\{5,1\}$ (Figure 5), respectively. The energy of activation is 4.2−4.6 kcal/mol, depending on the basis set employed (Table 4). The changes in bond length occuring during the transformation from reactant to transition state complex, expressed by the Δ values (Table 5), show an expansion during the reaction and thus verifies a dissociative mechanism. The operation of an I_d mechanism was studied by means of eq 2. Seven water molecules, six water molecules in the first coordination sphere and one as incoming/outgoing ligand, are required. The only transition state that meets this requirement is complex $\{5,2\}^{\#}$ (Figure 6). The pathway of the leaving water molecule lies in the mirror plane bisecting the complex, and thus, only one hydrogen bond to water molecules in the first coordination sphere exists. The same basis set dependence shown previously for complex $\{5,1\}^{\#}$ was found for this complex, and therefore, the same limitations concerning the reliabiltiy of this complex have to be considered. Although complex $\{5,2\}^{\#}$ might be questionable and can be interpreted as artifact of the basis set and the assumption within the model used, it shows that the seventh water molecule does not penetrate the first coordination sphere of Zn^{2+} but rather stays in the second coordination sphere. At the same time, the leaving water molecule is moved to the frontier of the first and second coordination sphere. As a whole, this structure rather resembles a hydrated transition state $\{5,1\}^{\#}$ found for a limiting dissociative mechanism than a transition state for an I_d mechanism. Consideration of the energy of activation (Table 4), which is only 1 kcal/mol less than the corresponding energy for the D mechanism and the Δ value (Table 5), which is almost equal to the one found for eq 1, further supports this statement. Therefore, within the model presented, an I_d mechanism for the water exchange reaction on Zn^{2+} could not be found and a D mechanism for this reaction is most likely.

We are aware of the fact that the model for the water exchange reaction presented in this paper has limitations and that the results cannot be transferred rigorously to solution. We are now studying 12 water molecules in the second coordination sphere of $[Zn(H_2O)_6]^{2+}$. Preliminary computations show that, due to the complexity of the resulting system, either solvent reaction field calculations or a combination of molecular orbital and molcular dynamic computations are necessary in order to simulate the movement of water molecules between first and second coordination sphere and hence the water exchange behavior of Zn^{2+}.

Supporting Information Available: Figures 1 and 4−7, cartesian coordinates, total energies, zero-point energies, and frequencies of all structures described in the text as archive entries produced by Gaussian 94; Tables 2 and 4; total energies, zero-point energies [au] and results from additional basis set modifications (SHA2 and SHA3) as Tables 2_sup and 4_sup; Figure 3; plots of all calculations as Figure 3_sup; Chapter 2b, detailed description of the computational techniques and basis sets used; Chapter 3a and 3b, detailed discussion of the basis set dependency (78 pages). See any current masthead page for ordering and Internet access instructions.

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