Inorganic Chemistry

Article

Searching for Stable, Five-Coordinate Aquated Al(III) Species. Water Exchange Mechanism and Effect of pH

Hans Hanauer,[†,‡] Ralph Puchta,[†,‡] Timothy Clark,[‡] and Rudi van Eldik*,[†]

Institute for Inorganic Chemistry, University of Erlangen-Nürnberg, Egerlandstrasse 1, 91058 Erlangen, Germany, and Computer Chemistry Center, University of Erlangen-Nürnberg, Nägelsbachstrasse 25, 91052 Erlangen, Germany

Density functional theory calculations have been performed for the water exchange mechanism of aquated Al(III). The effect of pH was considered by studying the exchange processes for $[Al(H_2O)_6]^{3+}$ and its conjugated base, $[Al(H_2O)_5OH]^{2+}$. Both complexes were found to exchange water in a dissociative way with activation energies (E_A) of 15.9 and 10.2 kcal/mol, respectively. The influence of solvent molecules on the gas-phase cluster model was considered by the addition of up to four water molecules to the model system. The stabilizing effect of the solvent on the transition state decreases E_A to 8.6 (hexa-aqua complex) and 7.6 (monohydroxo complex) kcal/mol, whereas E_A for all hydroxo species is consistently significantly lower than those for the related aqua systems, which indicates a much faster water exchange rate. For the hydroxo complex, all calculated five-coordinate intermediates, $nH_2O \cdot [Al(H_2O)_4(OH)]^{2+}$ ($n = 1, 2, 3, 4, 5$), are more stable than the corresponding six-coordinate reactants. Our results therefore suggest the presence of a stable five-coordinate species of aquated Al(III), namely, the $[Al(H_2O)_4(OH)]^{2+}$ complex.

Introduction

Aquated Al(III) species are important and interesting because of their frequent occurrence in nature, for example, in clays or hydroxide phases,[1,2] their high toxicity to plants and humans,[3,4] and their rich variety of solute structures.[5,6] Despite the species' ubiquitous nature, details of the coordination sphere of aquated Al(III) are still unresolved, especially in the biochemically relevant pH range from 4.3 to 7.0 in which a shift from the preferred six- to the fourfold coordination occurs. A recent study[7] provided evidence for the first time for a stable, five-coordinate aquated Al(III)

species, namely, $[Al(H_2O)_4OH]^{2+}$. The authors used high-pressure ^{17}O NMR techniques and Car–Parrinello molecular dynamics[8] (CPMD) to study the hydrogen-ion-concentration dependence of the water exchange process.

A mechanistic understanding of solvent exchange reactions of solvated metal ions is of fundamental importance for the general understanding of ligand substitution processes, especially since, in many cases, biological and catalytic reactions are controlled by the lability of coordinated solvent molecules. For this reason, much work has been devoted to the elucidation of these reaction mechanisms, not only to understand the underlying mechanisms but also to especially develop knowledge that will enable systematic control over and modification of such processes. Our understanding of solvent exchange mechanisms has benefited substantially in recent years from the use of sophisticated high-pressure kinetic techniques such as NMR line broadening[9–11] and from theoretical calculations[12–15] on the nature of the transition

* To whom coresspondence should be addressed. E-mail: vaneldik@chemie.uni-erlangen.de.
† Institute for Inorganic Chemistry.
‡ Computer Chemistry Center.

(1) Tyantova, E. N.; Burukhin, S. B.; Synzynys, B. I.; Koz'min, G. V. *Agrokhimiya* **2005**, 87.
(2) Zatta, P., Ed. Recent Topics in Aluminium Chemistry. *Coord. Chem. Rev.* **2002**, *228* (2) (308 pp).
(3) Mossor-Pietraszewska, T. *Acta Biochim. Pol.* **2001**, *48*, 673.
(4) Monteagudo, F. S.; Cassidy, M. J.; Folb, P. I. *Med. Toxicol. Adverse Drug Exper.* **1989**, *4*, 1.
(5) Casey, W. H. *Chem. Rev.* **2006**, *106*, 1.
(6) Casey, W. H.; Phillips, B. L.; Furrer, G. *Rev. Mineral. Geochem.* **2001**, *44*, 167.
(7) Swaddle, T. W.; Rosenqvist, J.; Yu, P.; Bylaska, E.; Phillips, B. L.; Casey, W. H. *Science* **2005**, *308*, 1450.

(8) Car, R.; Parrinello, M. *Phys. Rev. Lett.* **1985**, *55*, 2471.
(9) Helm, L.; Merbach, A. E. *Chem. Rev.* **2005**, *105*, 1923.
(10) van Eldik, R.; Hubbard, C. D. In *Chemistry at Extreme Conditions;* Riad Manaa, M., Ed.; Elsevier: Amsterdam, The Netherlands, 2005; Chapter 4, pp 109–164.
(11) Richens, D. T. *Chem. Rev.* **2005**, *105*, 1961.
(12) Rotzinger, F. P. *Chem. Rev.* **2005**, *105*, 2003.

state involved in such processes.[16] Volumes of activation obtained from the pressure dependence of the solvent exchange process have been demonstrated to possess an exceptional mechanistic discrimination ability.[17,18] A recent review by Lincoln shows, in a semi-historical way, the establishment of the nature of aquated metal ions and of water exchange and ligand substitution processes on them.[19]

One important aspect is the influence of pH on water exchange reactions in general. A number of studies have been devoted to this topic, and it is now well-documented that the deprotonation of aquated metal ions such as $[Fe(H_2O)_6]^{3+}$, $[Rh(H_2O)_6]^{3+}$, and $[Ir(H_2O)_6]^{3+}$ to form the corresponding monohydroxo $[M(H_2O)_5OH]^{2+}$ complexes not only leads to a drastic increase in the water exchange rate constant but also causes a changeover in the underlying reaction mechanism from a more associative (A) to a more dissociative (D) process induced by the trans effect of the coordinated hydroxide ion.[20] In an earlier study, we demonstrated, using density functional theory (DFT), that the deprotonation of $[Ti(H_2O)_6]^{3+}$ causes a changeover in the water exchange mechanism from a limiting A mechanism to a limiting D mechanism for the $[Ti(H_2O)_5OH]^{2+}$ complex ion.[21] In principle, a D mechanism will proceed via a five-coordinate transition state and could involve the formation of a stable, five-coordinate intermediate, as found for aquated Al(III) mentioned above.

We have now extended this work to solvent exchange reactions on $[Al(H_2O)_6]^{3+}$ and $[Al(H_2O)_5OH]^{2+}$. For the former complex, experiment and theory have so far shown that the $[Al(H_2O)_6]^{3+}$ ion exchanges water according to a dissociative interchange (I_d) mechanism characterized by an activation volume of $+5.2$ cm^3 mol^{-1}.[22,23] Deprotonation of $[Al(H_2O)_6]^{3+}$ has been reported to cause an increase of approximately 10^4 in the water exchange rate constant.[24] The challenge now, in light of the recent findings mentioned above, is to search for theoretical evidence for the formation of five-coordinate transition state and intermediate species as an integrated part of the water exchange process on aquated Al(III). The work reported here shows under which conditions evidence for such species can be found, whereby the pH of the solution and the nature of the solvent sphere selected are the controlling factors.

Mechanistic Approach

Until now, the solvation sphere around hydrated metal ions has usually only been considered explicitly for the first and to some extent for the second coordination spheres (usually for only one additional water molecule). Only a few studies exist in which pure quantum-mechanical methods have been used to take a complete second coordination sphere for aquated metal ions into consideration.[25] Most simulations of ligand exchange processes or the solvent organization around a metal center have used pure classical molecular dynamics (MD) simulations,[26−31] mixed quantum mechanics/molecular mechanics (QM/MM) approaches,[26,32−34] or CPMD simulations.[7,35−40] These methods were successfully used to study the behavior and dynamics of a metal ion in solution but only in a few cases to explore the details of a ligand exchange mechanism because of the rare-event problem and general methodic limitations.[15] To our knowledge, only a very fast water exchange around Ca^{2+} [41] and Sr^{2+} [42] was observed during unconstrained CPMD simulations. An overview of widely used computational methods is given in recent reviews.[12,43]

The explicit consideration of a second coordination sphere leads to special problems related to the determination of the number and the orientation of the coordinated water molecules. In addition, for a large number of water molecules around a metal center, one can expect a large number of conformations to be local minima, such that a variety of pathways for solvent exchange processes will be possible, depending on the starting structure selected for the simulation. This can lead to biased mechanistic conclusions, as we will show later. Generally, even for a second or third solvation sphere, the concentration of the solvated metal ion

(13) Puchta, R.; Galle, M.; van Eikema Hommes, N.; Pasgreta, E.; van Eldik, R. *Inorg. Chem.* **2004**, *43*, 8227.
(14) Puchta, R.; van Eikema Hommes, N.; van Eldik, R. *Helv. Chim. Acta* **2005**, *88*, 911.
(15) Erras-Hanauer, H.; Clark, T.; van Eldik, R. *Coord. Chem. Rev.* **2003**, *238−239*, 233.
(16) Helm, L.; Merbach, A. E. *Coord. Chem. Rev.* **1999**, *187*, 151.
(17) Drljaca, A.; Hubbard, C. D.; van Eldik, R.; Asano, T.; Basilevsky, M. V.; Le Noble, W. J. *Chem. Rev.* **1998**, *98*, 2167.
(18) Stochel, G.; van Eldik, R. *Coord. Chem. Rev.* **1999**, *187*, 329.
(19) Lincoln, S. E. *Helv. Chim. Acta* **2005**, *88*, 523.
(20) Cusanelli, A.; Frey, U.; Richens, D. T.; Merbach, A. E. *J. Am. Chem. Soc.* **1996**, *118*, 5265.
(21) Hartmann, M.; Clark, T.; van Eldik, R. *J. Phys. Chem. A* **1999**, *103*, 9899.
(22) Kowall, T.; Caravan, P.; Bourgeois, H.; Helm, L.; Rotzinger, F. P.; Merbach, A. E. *J. Am. Chem. Soc.* **1998**, *120*, 6569.
(23) Hugi-Cleary, D.; Helm, L.; Merbach, A. E. *Helv. Chim. Acta* **1985**, *68*, 545.
(24) Nordin, J. P.; Sullivan, D. J.; Phillips, B. L.; Casey, W. H. *Inorg. Chem.* **1998**, *37*, 4760.
(25) Yang, T.; Bursten, B. E. *Inorg. Chem.* **2006**, *45*, 5291.
(26) Loeffler, H. H.; Inada, Y.; Funahashi, S. *J. Phys. Chem. B* **2006**, *110*, 5690.
(27) Spångberg, D.; Rey, R.; Hynes, J. T.; Hermansson, K. *J. Phys. Chem. B* **2003**, *107*, 4470.
(28) Hermansson, K.; Wojcik, M. *J. Phys. Chem. B* **1998**, *102*, 6089.
(29) Spångberg, D.; Wojcik, M.; Hermansson, K. *Chem. Phys. Lett.* **1997**, *276*, 114.
(30) Lauenstein, A.; Hermansson, K.; Lindgren, J.; Probst, M.; Bopp, P. A. *Int. J. Quantum Chem.* **2000**, *80*, 892.
(31) Spångberg, D.; Hermansson, K. *J. Chem. Phys.* **2004**, *120*, 4829.
(32) Schwenk, C. F.; Loeffler, H. H.; Rode, B. M. *J. Am. Chem. Soc.* **2003**, *125*, 1618.
(33) Inada, Y.; Mohammed, A. M.; Loeffler, H. H.; Rode, B. M. *J. Phys. Chem. A* **2002**, *106*, 6783.
(34) Schwenk, C. F.; Loeffler, H. H.; Rode, B. M. *Chem. Phys. Lett.* **2001**, *349*, 99.
(35) Pasquarello, A.; Petri, I.; Salmon, P. S.; Parisel, O.; Car, R.; Toth, E.; Powell, D. H.; Fischer, H. E.; Helm, L.; Merbach, A. E. *Science* **2001**, *291*, 856.
(36) Buehl, M.; Kabrede, H. *Inorg. Chem.* **2006**, *45*, 3834.
(37) Buehl, M.; Kabrede, H.; Diss, R.; Wipff, G. *J. Am. Chem. Soc.* **2006**, *128*, 6357.
(38) Buehl, M.; Diss, R.; Wipff, G. *J. Am. Chem. Soc.* **2005**, *127*, 13506.
(39) Amira, S.; Spångberg, D.; Hermansson, K. *J. Chem. Phys.* **2006**, *124*, 104501.
(40) Amira, S.; Spångberg, D.; Hermansson, K. *Phys. Chem. Chem. Phys.* **2005**, *7*, 2874.
(41) Naor, M. M.; van Nostrand, K.; Dellago, C. *Chem. Phys. Lett.* **2003**, *369*, 159.
(42) Harris, D. J.; Brodholt, J. P.; Sherman, D. M. *J. Phys. Chem. B* **2003**, *107*, 9056.
(43) Rode, B. M.; Schwenk, C. F.; Hofer, T. S.; Randolf, B. R. *Coord. Chem. Rev.* **2005**, *249*, 2993.

Scheme 1. Schematic Energy Profile and Structures for the Associative (A) Water Exchange Mechanism and the Abbreviations Used in the Text

for X = H$_2$O: (6,1)	(7,0)‡	(7,0)	(7,0)‡	(6,1)
for X = OH⁻ (5,OH,1)	(6,OH)‡	(6,OH)	(6,OH)‡	(5,OH,1)
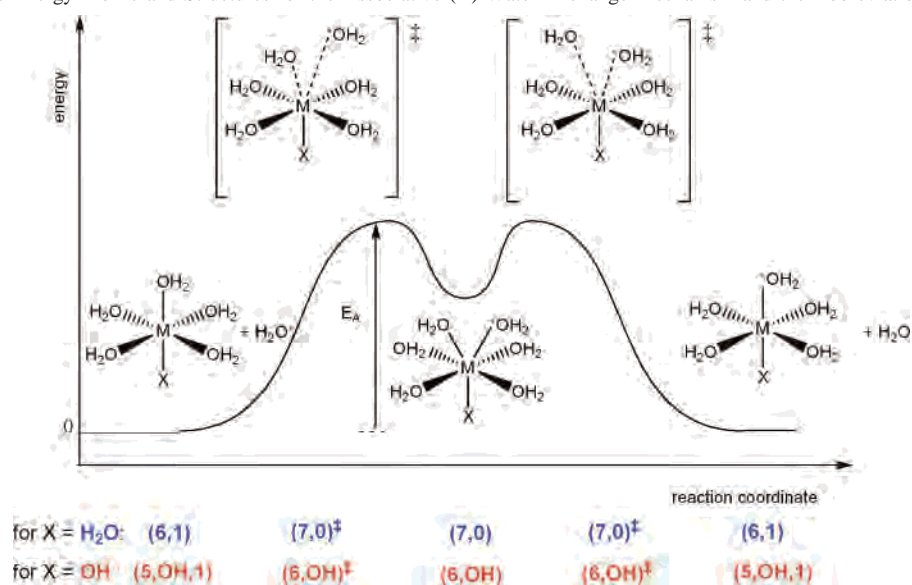
Scheme 2. Schematic Energy Profile and Structures for the Interchange (I) Water Exchange Mechanism and the Abbreviations Used in the Text

|		
for X = H$_2$O· (6,1)	(5,2)‡	(6,1)
for X = OH⁻ (5,OH,1)	(4,OH,2)‡	(5,OH,1)
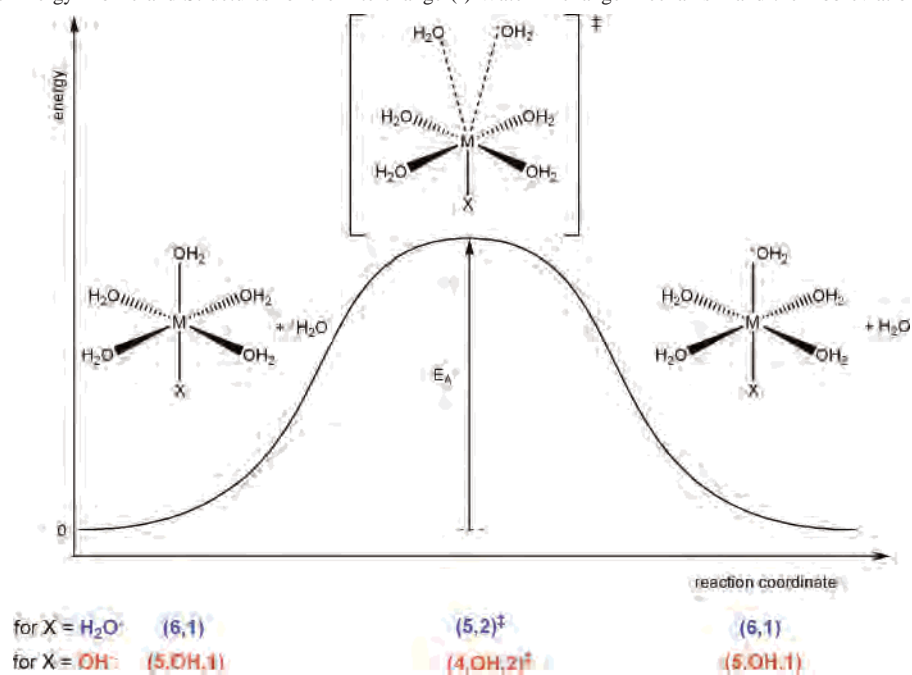
would be far too high to compare with realistic experimental conditions for the classical ab initio/DFT cluster−solvent approach and also for the widely used periodic boundary conditions in CPMD studies. Of course, the final goal is to obtain simulations as close as possible to the real system. Well aware of the limitations of the different methods, we will report in this work the influence of additional water molecules on the energy and reaction mechanism by considering six water molecules in the first coordination sphere and stepwise up to four in the second coordination sphere as an approach to gain further insight into the cluster−solvent interaction of the exchange process.

Selected Model Reactions. The water exchange mechanism of hydrated Al(III) was examined using gas-phase clusters consisting of the metal ion surrounded by different numbers of water molecules. To model the influence of pH on the reaction mode, one water was substituted by a hydroxo ligand. Within this computational−mechanistic study, the following theoretically possible substitution mechanisms, namely, limiting A (Scheme 1), A/D interchange (I, Scheme 2), and limiting D (Scheme 3), were analyzed in order to find the most favorable reaction pathway.

According to the mechanistic models, the limiting A and limiting D pathways are characterized by the formation of stable seven- or five-coordinate intermediates, respectively, followed by the reverse process, which involves an identical transition state because the reaction is symmetrical. In contrast, an I mechanism involves only one transition state, in which concerted ligand exchange appears to lead directly to the product species.

Notation. In order to describe the complexes consistently, the following notation was adopted. Bond lengths are

Scheme 3. Schematic Energy Profile and Structures for the Dissociative (D) Water Exchange Mechanism and the Abbreviations Used in the Text

| for X = H$_2$O: | (6,0) | (5,1)‡ | (5,1) | (5,1)‡ | (6,0) |
| for X = OH$^-$: | (5,OH) | (4,OH,1)‡ | (4,OH,1) | (4,OH,1)‡ | (5,OH) |
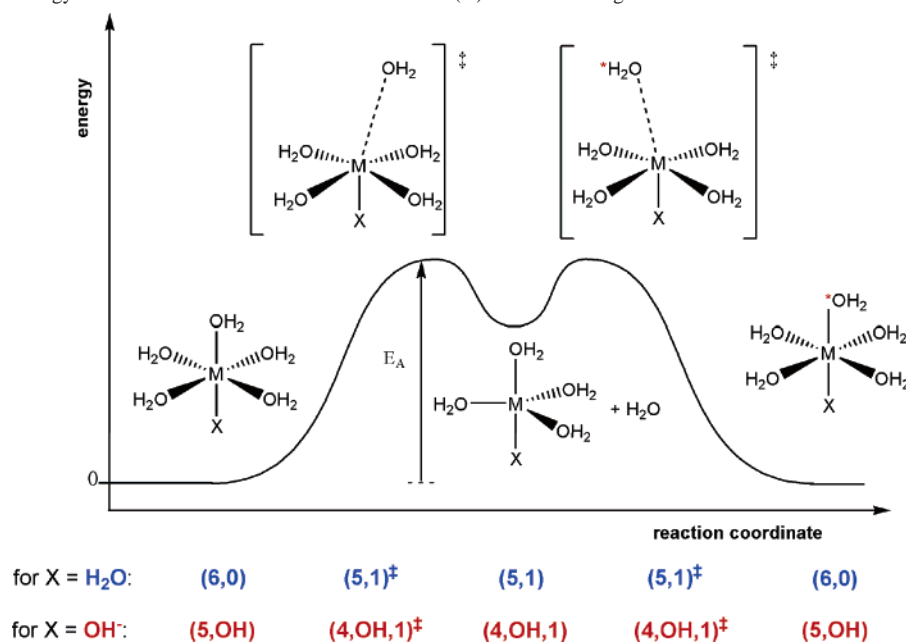
abbreviated as r(Al−O) [Å] with the indices I and II indicating the first and second coordination spheres, respectively. The exchanging water molecules in the transition states are indicated with both indices. The complexes [Al-(H$_2$O)$_n$]$^{3+}$·mH$_2$O, where n = 4, 5, 6, and 7 and m = 0, 1, 2, 3, 4, and 5 are abbreviated only by their coordination numbers in the first and second coordination spheres, leading to an (n,m) notation, for example, (6,0) for the hexa-aqua complex. This notation is used in the same way for the hydroxo complexes, for example, (5,OH,0) for the [Al(H$_2$O)$_5$-(OH)]$^{2+}$ complex. See the descriptions included in Schemes 1, 2, and 3.

Computational Details. All structures were fully optimized at the B3LYP/6-311+G** level[44−47] and characterized as minima or transition states by computation of the normal vibrations within the harmonic approximation. All energies are corrected for zero-point energies (ZPE). The Gaussian 03 suite of programs was used throughout.[48]

Results and Discussion

Associative Mechanism. For the chosen level of theory, all attempts to coordinate a seventh water molecule to the aquated Al(III) center for both the hexa-aqua and the penta-aquahydroxo complexes were unsuccessful. All DFT calculations for a sevenfold coordinated Al(III), Al(7,0), ended up in a sixfold coordination with the seventh water molecule located in the second coordination sphere. Depending on the starting structure, we found that this second sphere water molecule can be bound either in a bifurcated way through two hydrogen bonds to two first sphere water ligands, which

Scheme 4 Two Possible Coordination Modes (Linear and Bifurcated) of External Water Molecules^a
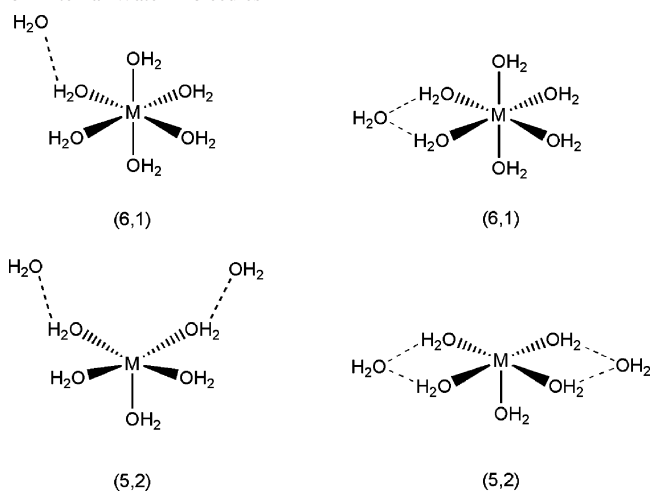
^{a} The structures on the left are higher in energy because of the presence of a single hydrogen bond to the external water molecules.

is practically identical to the (6,1) structure used as the reactant structure for the D mechanism, or in a linear way through only one hydrogen bridge (see Scheme 4). This

(44) Stevens, P. J.; Devlin, F. J.; Chablowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.
(45) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
(46) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
(47) Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory,* 2nd ed.; Wiley−VCH: Weinheim, Germany, 2002; p 528.

(48) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.
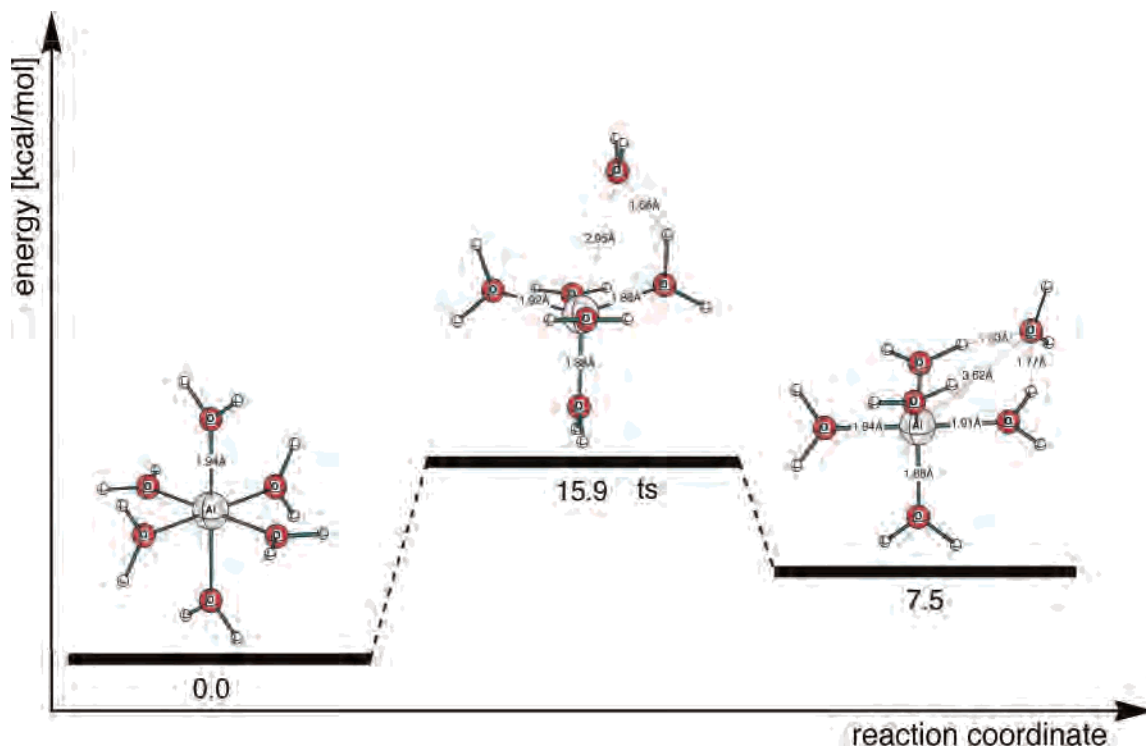
Figure 1. Calculated (B3LYP/6-311+G**) energy profile and selected bond lengths for water exchange on $[Al(H_2O)_6]^{3+}$.

structure is higher in energy and can be considered to be a pre-equilibrium structure in terms of the water exchange process. Therefore, in agreement with available experimental data, we conclude that an A water exchange mechanism, which demands a seven-coordinate intermediate, can be excluded for aquated Al(III).

Interchange Mechanism. The I mechanism demands a transition state with weak coordination of the two exchanging water molecules. Depending on the A or D character of the I process, these water molecules are somewhere between the first and the second coordination spheres or in the region of the second coordination sphere. All our attempts to locate such a transition state failed, most likely because of the omission of the complete second (or higher) coordination sphere. The $Al-O_{I/II}$ interaction is so weak that H-bonding to the hydrogen atoms of the equatorial water ligands is favored. Similar results were obtained by Rotzinger for the solvent exchange of trivalent transition metal ions and are due to an incorrectly balanced description of the metal−ligand and hydrogen-bond strengths by DFT.[49] However, we failed to calculate the transition state structure for the I mechanism even in the cluster model with four additional water molecules, where no hydrogens in the first coordination sphere are available for hydrogen bonding without breaking an existing one. Therefore, all calculations resulted in structures where the exchanging water molecules were either coordinated in a linear way to the equatorial aqua ligands or coordinated in a bifurcated way (see Scheme 4). Within the selected model, we are not able to corroborate the experimentally favored I_d mechanism.[23]

We attribute the absence of the A and I types of exchange mechanism not to the limitations of DFT but to the small ionic size (53 pm) in combination with the charge-driven coordination of six water molecules around the Al(III) ion. This is corroborated by comparison with our recent calculations for Li(I). The naked Li^+ ion is 50% larger than naked Al^{3+} and is only five-coordinate during the water exchange process.[13] Even for the larger Ga^{3+} ion (62 pm), both the experimental ^{17}O NMR data[50] and the theoretical calculations[22] suggest a dissociatively activated exchange process.

Dissociative Mechanism. The most favored gas-phase structure of $[Al(H_2O)_6]^{3+}$ has T_h symmetry (Figure 1) with a metal−oxygen bond length of 1.94 Å. This value is in good agreement with results obtained by Wassermann et al.,[51] who calculated a range of 1.90−1.95 Å for the Al−O bond (also in T_h symmetry) using MP2 with correlation consistent basis sets of double and triple ξ quality. Bock et al. reported for different basis sets values of 1.90−1.91 Å (SVWN5), 1.95−1.96 Å (BLYP), 1.93−1.94 Å (B3LYP), 1.92−1.93 Å (HF), and 1.92−1.93 Å (MP2).[52] The MP2/6-311+G** value is 1.93 Å,[53] whereas 1.90 Å was found in solution from experimental X-ray data.[54] Detaching one of the coordinated water molecules leads to the transition state for the D pathway. The leaving water molecule forms a hydrogen

(49) Rotzinger, F. P. *J. Phys. Chem. B* **2005**, *109*, 1510.

(50) Hugi-Cleary, D.; Helm, L.; Merbach, A. E. *J. Am. Chem. Soc.* **1987**, *109*, 4444.
(51) Wasserman, E.; Rustad, J. R.; Xantheas, S. S. *J. Chem. Phys.* **1997**, *106*, 9769.
(52) Bock, C. W.; Markham, G. D.; Katz, A. K.; Glusker, J. P. *Inorg. Chem.* **2003**, *42*, 1538.
(53) Kubicki, J. D.; Sykes, D.; Apitz, S. E. *J. Phys. Chem. A* **1999**, *103*, 903.
(54) Bol, W.; Welzen, T. *Chem. Phys. Lett.* **1977**, *49*, 189.

Table 1. Selected Structural Parameters for the D Pathway and Relative Energies (kcal/mol) of the Hexa-Aqua Complexes

complex	$r(Al-O_I)$ [Å]	$r(Al-O_{II})$ [Å]	ΔE	ΔG^c	$\sum r(Al-O)^d$ [Å]	PG
(6,0)	1.94				11.64	T_h
(5,1)‡	1.88, 1.92, 1.91, 1.91, 1.86	2.95	15.9^a	13.5	12.43	C_1
(5,1)	1.88, 1.88, 1.91, 1.94, 1.84	3.62	7.5^b	4.2	13.07	C_1
(6,1)	1.96, 1.92, 1.91, 1.95, 1.95, 1.96	3.69			15.33	C_1
(5,2)‡	1.90, 1.86, 1.9, 1.87, 1.93	3.66, 2.84	11.5^a	11.4	15.96	C_1
(5,2)	1.89, 1.85, 1.91, 1.85, 1.91	3.65, 3.65	0.2^b	0.3	16.72	C_2
(6,2)	1.93, 1.93, 1.93, 1.93, 1.96, 1.96	3.70, 3.70			19.03	C_2
(5,3)‡	1.91, 1.89, 1.92, 1.88, 1.85	2.87, 3.72, 3.67	8.3^a	8.0	19.71	C_1
(5,3)	1.89, 1.85, 1.90, 1.85, 1.89	3.66, 3.66, 3.67	−1.3^b	−1.4	20.38	C_1
(6,3)	1.97, 1.97, 1.925, 1.91, 1.91, 1.92	3.71, 3.71, 3.71			22.73	C_1
(5,4)‡	1.91, 1.88, 1.86, 1.89, 1.87	2.85, 3.64, 3.68, 3.68	10.45	10.9	23.26	C_1
(5,4)	1.90, 1.85, 1.88, 1.85, 1.88	3.67, 3.67, 3.67, 3.67	−1.6	−2.0	24.05	C_1
(6,4)	1.99, 1.99, 1.90, 1.90, 1.90, 1.90	3.69, 3.70, 3.69, 3.70			26.35	C_2
(5,5)‡	1.90, 1.88, 1.86, 1.87, 1.86	3.33, 3.70, 3.67, 3.58, 3.68	13.5	13.1	27.31	C_1
(5,5)	1.90, 1.88, 1.85, 1.88, 1.85	5.61, 3.68, 3.68, 3.56, 3.68	4.2	2.7	29.56	C_1

^{a} Energy of activation. ^{b} Reaction energy. ^{c} Including thermal energy correction $G = H - TS = E + RT - TS$. ^{d} Sum of all aluminum−oxygen bond lengths.

bridge, $r(O-H) = 1.66$ Å, to one of the coordinated water molecules and is located between the first and the second coordination spheres at a distance of 2.95 Å to the metal center. The bond trans to the leaving water, $r(Al-O_I)$, is shortened to 1.88 Å, similar to the 1.86 Å for the water molecule offering the hydrogen bridge, which causes a higher acidity. The remaining water molecules stay relatively unchanged at distances between 1.91 Å and 1.92 Å. Such structures are also found for other aquated metal ions, for example, $\{[Ni(H_2O)_5\cdots H_2O]^{2+}\}^{\ddagger}$ [55] or $\{[Ti(H_2O)_4(OH)\cdots H_2O]^{2+}\}^{\ddagger}$ [21]. In the intermediate structure, the leaving water molecule becomes part of the second coordination sphere at a distance of 3.62 Å to the Al(III) center. The pre-existing H-bond becomes stronger and decreases to 1.53 Å, and a weaker second hydrogen bridge is formed ($r(O-H) = 1.77$ Å). The coordination sphere during this D process changes from a highly symmetrical octahedral, via a distorted octahedral in the transition state, to a trigonal-bipyramidal intermediate, distorted by the coordination of the leaving water molecule. Therefore, the equatorial Al−O bond lengths decrease to 1.88, 1.88, and 1.84 Å, respectively, whereas the axial bond lengths remain longer at 1.94 and 1.91 Å, respectively. In both cases, the shorter distances are caused by the hydrogen bridges formed. The activation energy for this D water exchange process was calculated to be 15.9 kcal/mol (Table 1).

Upon including one additional water molecule for this reaction (Figure S1, Supporting Information), the activation energy decreases to 11.5 kcal/mol. This additional water molecule is initially located in the second coordination sphere at a distance of 3.69 Å to the metal center, fixed through two H-bonds in a bifurcated way ($r(H-O) = 1.73$ and 1.68 Å). The two water ligands involved in the H-bonds are slightly closer to the Al(III) center (1.92 and 1.91 Å), whereas the remaining water ligands stay almost unchanged relative to the T_h structure (1.94 Å). The slight decrease in $r(Al-O_{II})$ from 3.69 to 3.66 Å and the frequency analysis of the single imaginary frequency in the transition state show that it is not directly involved in the exchange process but has a significant influence on E_A. Not only is the transition state

(55) Rotzinger, F. P. *J. Am. Chem. Soc.* **1996**, *118*, 6760.

stabilized, but also the overall reaction energy is reduced to 0.2 kcal/mol which means that the reactant and intermediate are practically of the same energy. In other words, the five-coordinate Al(III) in (5,2) becomes more favorable than in the (5,1) complex. Compared to (5,1)‡, the leaving water in the transition state (5,2)‡ is only 2.84 Å away from the metal center (i.e., 0.11 Å closer) but has a weaker hydrogen bond (1.75 vs 1.66 Å). The $r(Al-O_I)$ becomes only slightly shorter, except for two particular water ligands: the one in the trans position to the leaving water and the one donating the hydrogen bridge (Table 1). In the intermediate‡ structure (5,2), the two $r(Al-O_{II})$ bonds average 3.65 Å, and a second H-bond to the leaving water is formed.

On going to the reaction (6,2) → (5,3) (Figure S2, Supporting Information), the activation barrier and the reaction energy both decrease. The barrier is reduced to 8.3 kcal/mol, and the reaction energy is reduced to −1.3 kcal/mol. This is once more due to a stabilization of the transition state and the five-coordinate intermediate in comparison to the six-coordinate reactant as a result of a second sphere chelation effect. In the C_2 symmetric (6,2) structure, all equatorial water ligands have $r(Al-O_I)$ values of about 1.92 Å, whereas the axial ones are slightly longer at 1.96 Å. The bifurcated external water molecules are at distances of 3.70 Å to the metal center. The rotation of an equatorial water ligand in the transition state (5,3)‡, while breaking a H-bond, donates the H-bond to stabilize the leaving water, $r(Al-O_{II}) = 2.87$ Å. The extremely short H-bond, $r(O-H) = 1.28$ Å, to the former bifurcated bound second sphere water is exceptional. In the case of the reaction (6,3) → (5,4) (Figure S3, Supporting Information), the trend in the activation energies reverses, and a barrier of 10.5 kcal/mol is found. However, in contrast, the intermediate is 1.6 kcal/mol more stable than the reactant. The structural parameters are in the expected range and are summarized in Table 1.

The (6,4) system represents a distinct situation, see Figure 2. It consists of four water molecules at a distance of 3.70 Å to the Al(III) center. These external waters are bound in a bifurcated way ($r(O-H) = 1.80$ to 1.81 Å) to the equatorial water ligands. Thus, there are no protons available to donate a H-bond to the leaving water molecule in the transition state
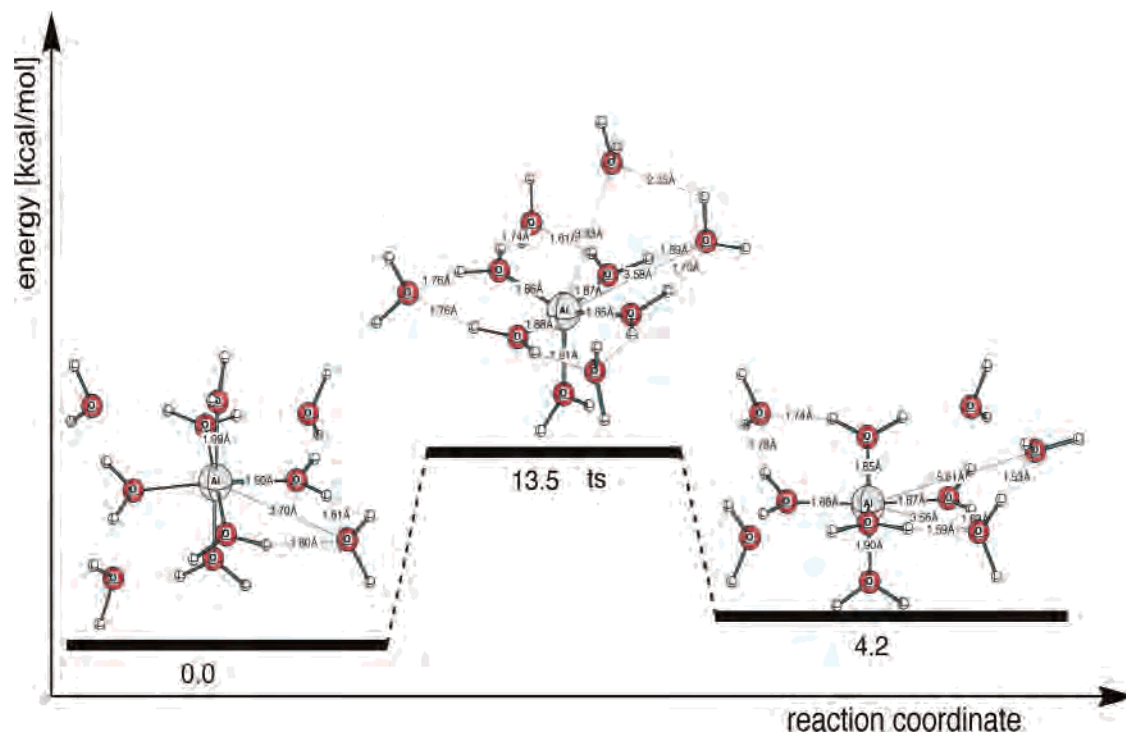
Figure 2. Calculated (B3LYP/6-311+G**) energy profile and selected bond lengths for water exchange on $[Al(H_2O)_6]^{3+}$ with explicit consideration of four additional water molecules.

Table 2. Selected Structural Parameters for the D Pathway and Relative Energies (kcal/mol) of the Monohydroxo Complexes

complex	$r(Al-O_I)$ [Å]	$r(Al-O_{II})$ [Å]	$r(Al-OH)$ [Å]	ΔE	ΔG	$\sum r(Al-O)^c$ [Å]	PG
(5,OH,0)	1.98, 1.99, 1.97, 1.97, 1.98		1.72			11.61	C_1
(4,OH,1)‡	1.95, 1.95, 1.95, 1.91	2.92	1.68	10.2^a	9.3	12.36	C_1
(4,OH,1)	1.96, 1.91, 1.96, 1.88	3.75	1.68	-1.1^b	-1.7	13.14	C_1
(5,OH,1)	1.97, 1.97, 1.98, 1.98, 2.00	3.79	1.73			15.40	C_1
(4,OH,2)‡	1.91, 1.93, 1.91, 1.96	2.86, 3.76	1.69	7.7^a	6.7	16.04	C_1
(4,OH,2)	1.89, 1.97, 1.88, 1.96	3.760, 3.760	1.69	-3.2^b	-3.5	16.90	C_1
(5,OH,2)	1.98, 1.98, 1.96, 1.96, 2.02	3.784, 3.728	1.73			19.14	C_1
(4,OH,3)‡	1.94, 1.92, 1.93, 1.92	2.91, 3.79, 4.17	1.70	3.4^a	3.7	20.27	C_1
(4,OH,3)	2.00, 1.90, 1.90, 1.87	4.21, 3.83, 3.98	1.69	-4.5^b	-7.3	21.38	C_1
(5,OH,3)	2.03, 1.96, 1.95, 1.95, 1.96	3.27, 3.78	1.76			22.38	C_1
(4,OH,4)‡	1.91, 1.93, 1.90, 1.93	2.80, 3.21, 3.73	1.73	3.7	3.4	22.93	C_1
(4,OH,4)	1.92, 1.92, 1.93, 1.92	3.69, 3.69, 3.79	1.67	-4.7	-6.7	24.30	C_1
(5,OH,4)	2.03, 1.96, 1.96, 1.96, 1.95	3.24, 3.69, 3.79, 3.77	1.77			26.11	C_1
(4,OH,5)‡	1.91, 1.93, 1.93, 1.91	3.00, 3.57, 3.63, 3.72, 3.68	1.71	6.1	4.7	26.99	C_1
(4,OH,5)	1.91, 1.93, 1.92, 1.92	5.87, 3.68, 3.68, 3.79, 3.70	1.70	-2.3	-5.4	30.09	C_1

^{a} Energy of activation. ^{b} Reaction energy. ^{c} Sum of all aluminum−oxygen bond lengths.

$(5,5)^{\ddagger}$, and this results in the longest distance for the leaving water to the metal center, namely, $r(Al-O_{I/II}) = 3.33$ Å, for all of the reactions studied. The water must form a H-bond to a second sphere water molecule, $r(O-H) = 2.35$ Å. Therefore, the increase in activation energy by 3.0 kcal/mol to 13.5 kcal/mol is more related to the structural influences or hindrance than to the properties of the metal center.

As a quantum-chemical descriptor for the volumes of activation, $\Delta V^{\ddagger}$, for these simulated reactions, we applied the method proposed by Rotzinger.[55] The volume descriptor "difference of sums of $r(Al-O_{I/II})$" decreases upon adding water molecules to the second coordination sphere. We calculated these values to be 0.79, 0.63, 0.68, 0.53, and 0.96 Å for going from (6,0) to (6,1), (6,2), (6,3), and (6,4) (Table 3), respectively. The latter value is related to the structural influence discussed above. The consistently positive values for all aqua complexes studied confirm the D character of

Table 3. Calculated Changes of the Volume Descriptor $\Delta\sum r$ for the D Water Exchange Process

model system	$\Delta\sum r(Al-O)^a$ [Å]	model system	$\Delta\sum r(Al-O)^a$ [Å]
(6,0)	0.79	(5,OH)	0.75
(6,1)	0.63	(5,OH,1)	0.86
(6,2)	0.68	(5,OH,2)	1.13
(6,3)	0.53	(5,OH,3)	0.55
(6,4)	0.96	(5,OH,4)	0.88

^{a} Approximated by the difference of the sum of all Al−O bond lengths between transition state and reactant.

the exchange process. The changes in the absolute values show no clear trend but remain of the same magnitude.

The somewhat lower values for the (6,1) and (6,2) systems may result from the structural stabilization caused by the second coordination sphere waters. The two coordinating water molecules are linked via a third to form a hydrogen-bonded chelate system and therefore limit the flexibility,
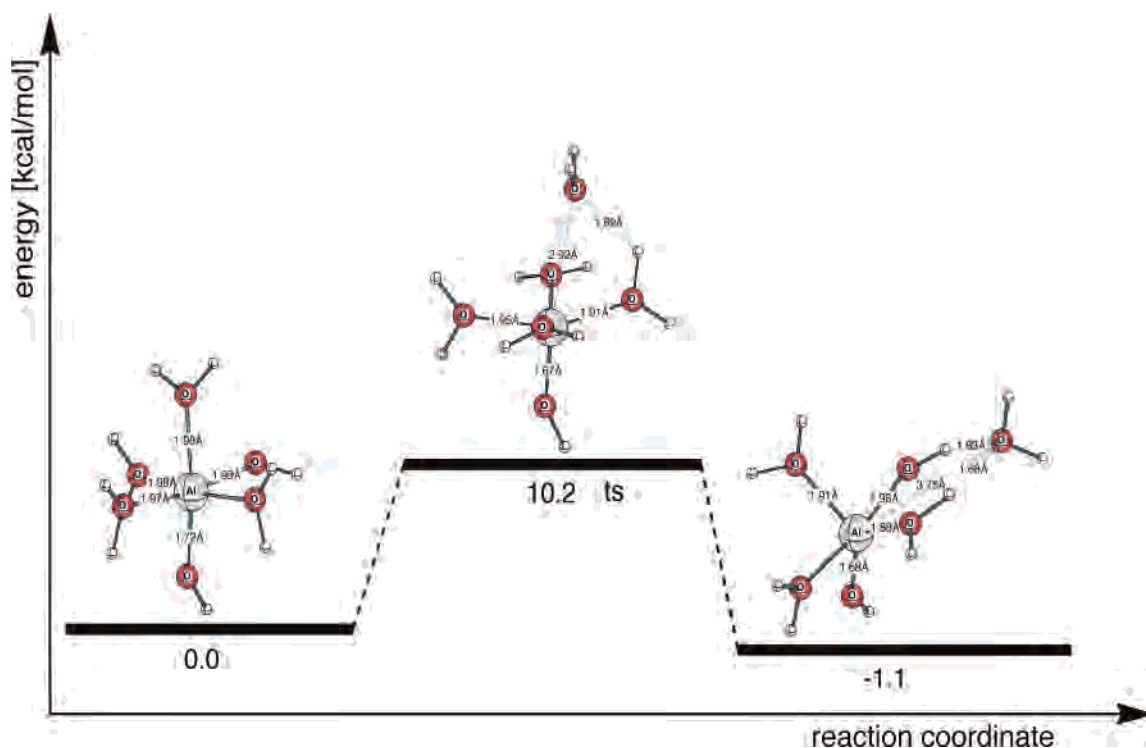
Figure 3. Calculated (B3LYP/6-311+G**) energy profile and selected bond lengths for water exchange on [Al(H$_2$O)$_5$(OH)]$^{2+}$.

possibly induce strain, and reduce the degree of freedom for rotation around the metal−oxygen bond in this complex compared to the pure hexa-aqua one.

Conjugated Base Species, Monohydroxo Complexes. From experimental data, we know that the water exchange rate for hydrated trivalent metals increases drastically with increasing pH,[22−24] and we therefore calculated the water exchange mechanism for the related monohydroxo complex in the same way as for the hexa-aqua complex.

Because of the negatively charged ligand and the resulting reduced overall charge on the (5,OH) complex as compared to the (6,0) complex, the structural properties are as expected: a short Al−OH bond and a longer r(Al−O$_I$), see Table 2. The r(Al−OH) value decreases from 1.72 Å in the reactant structure to 1.67 Å in the transition state (4,OH,1)‡, and the leaving water is located at a distance of 2.92 Å to the Al(III) center, 0.03 Å less than in (5,1)‡, and forms in a more axial position (∠HO−Al−O$_{I/II}$ = 173.8° and ∠H$_2$O− Al−O$_{I/II}$ = 166.3°) a significantly weaker H-bond (r(O$_{I/II}$− H) = 1.89 Å). In the intermediate (4,OH,1), r(Al−O$_{II}$) averages 3.75 Å, 0.13 Å longer than in (5,1). The two H-bonds to this water molecule are weaker with bond lengths of 1.83 and 1.68 Å, respectively (see Figure 3). These are, in general, characteristic for the hydroxo structures, namely, longer r(Al−O$_{II}$) and weaker H-bonds to the leaving water. The activation energy for the D water exchange process of (5,OH) is reduced to 10.2 kcal/mol which is 1/3 lower than that for (6,0). In contrast to (5,1), the five-coordinate (4,-OH,1) structure is stabilized with respect to (5,OH) without the additional influence of a solvent molecule. There are two main factors that affect not only the activation barrier but also the reaction energy (difference in energy between reactant and intermediate) which is −1.1 kcal/mol: the

labilizing effect of the hydroxo ligand (trans effect) and the reduced charge of the complex. This is observed for all hydroxo systems studied, as shown below.

The (5,OH,1) system behaves similarly, but the trans influence of the hydroxo ligand on the reactant structure is more distinct, r(Al−O$_{trans}$) = 2.00 Å (see Figure S4, Supporting Information). In the transition state, the bond to the leaving water is elongated by 0.86 Å, and this water forms an even weaker H-bond with r(O$_{I/II}$−H) = 2.00 Å. The H-bond donating water is 1.87 Å away from the metal center, and the second sphere water stays almost unchanged, equal to the corresponding hexa-aqua system. Both external water molecules in the intermediate are bifurcatedly H-bonded at a distance of 3.76 Å, in each case with one short r(Al−O$_I$) and one long one (1.88 and 1.95 Å). Just as for the corresponding hexa-aqua system, the activation energy decreases by 25% to 7.7 kcal/mol, but the intermediate is now 3.2 kcal/mol more stable than the reactant. Selected bond lengths and energies are given in Table 2.

Upon going to (5,OH,2), the trans influence causes a long r(Al−O$_{trans}$) = 2.02 Å and axial distortion. The angle between the axial ligands is bent to 170.4°, in contrast to (6,2) where it is fully linear. The Al(III) center lies approximately 8° below the plane formed by the four water ligands, and one of the external waters lies about 17° above this plane. The leaving water undergoes H-bonding with r(O$_{I/II}$−H) = 1.87 Å, 0.1 Å longer than in (5,3)‡ at a distance of 2.91 Å to Al(III). There is an additional weak H-bonding interaction to one external water, which is far above the equatorial position at a distance of 4.17 Å to the metal center, see Figure S5 (Supporting Information). This is in distinct contrast to (5,3)‡, where the corresponding water molecule is 0.25 Å closer and in an almost equatorial position (Figure S2). The
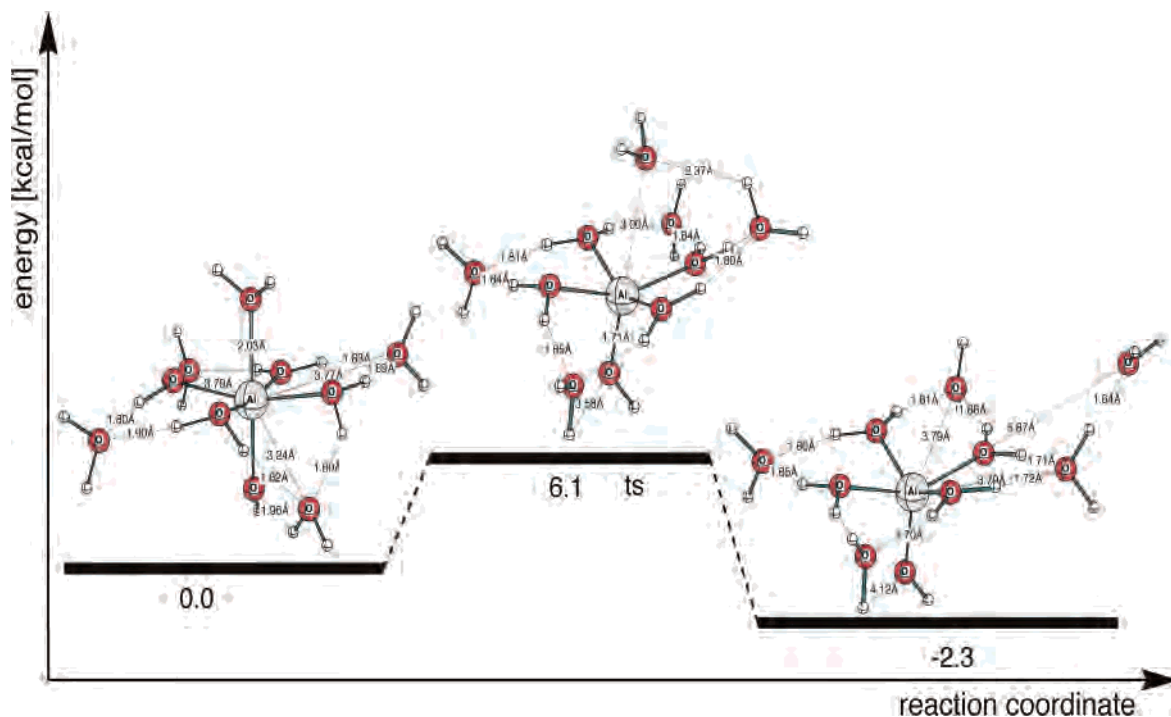
Figure 4. Calculated (B3LYP/6-311+G**) energy profile and selected bond lengths for water exchange on $[Al(H_2O)_5(OH)]^{2+}$ with explicit consideration of three additional water molecules.

higher electron density in the hydroxo species shifts the influence of the metal−oxygen interaction in favor of H-bonding. This can also be found in the intermediate, where only one external water is bound in a bifurcated way, and the remaining two form a single H-bond, $r(O_{II}−H) = 1.52$ and 1.55 Å, at distances of 3.98 and 4.21 Å, respectively. The H-bond interaction is so important that E_A is reduced to 3.4 kcal/mol, and remarkably, because of the two fewer H-bonds compared to the hexa-aqua case, the intermediate is 4.5 kcal/mol more stable than the reactant.

In the (5,OH,3) system (Figure 4), the third external water molecule is located far below (∼28°) the equatorial plane at a quite short distance of 3.27 Å to the metal center. It is fixed via three H-bonds; two of them are fixed to the equatorial water ligands, and one is fixed to the hydroxo ligand with bond lengths of 1.81, 1.84, and 2.03 Å, respectively. This structural element is conserved in the transition state with elongation of the $H_{H_2O}−O_{OH}$ H-bond to 2.16 Å but with shortening of the Al−O distance to 3.21 Å. During this reaction step, the distance to the water ligand in the trans position elongates from 2.03 to 2.80 Å, and this water is stabilized by a weak H-bond (2.02 Å). The intermediate consists of all four external waters in the equatorial plane with two shorter (3.69 Å) and two longer (3.79 Å) ligand−metal distances (Table 2). For this reaction, the energy of activation was found to be 3.7 kcal/mol, and a stable intermediate ($E_R = −4.7$ kcal/mol) is formed.

The (5,OH,4) system (Figure 5) once again shows the particular second sphere water that is below the equatorial plane and 3.24 Å away from the metal center. This is caused by three H-bonds as in (5,OH,3), with $r(H−O) = 1.80, 1.82,$ and 1.96 Å. The bond to the leaving water ligand in the trans position is elongated from 2.03 to 3.00 Å in the transition

state, which is 0.33 Å or 10% less than that for $(5,5)^{\ddagger}$ but 0.20 Å more than that in $(4,OH,4)^{\ddagger}$. It forms a H-bond with a second sphere water ligand, which is practically of the same strength as in $(5,5)^{\ddagger}$. The particular water molecule below the plane loses the axial H-bond, in contrast to $(4,OH,4)^{\ddagger}$, and converges to a more equatorial position, which is finally reached in the intermediate. Overall, during the first reaction step, two H-bonds are broken, one more than in $(5,5)^{\ddagger}$. Indeed, the energy of activation rises to 6.1 kcal/mol which is less than half that for the hexa-aqua system ($E_A = 13.5$ kcal/mol) but is significantly higher than that for the (5,-OH,3) system. The leaving water molecule becomes part of the second sphere at a distance of 5.87 Å to the metal center in the second step, 0.26 Å more than that for (5,5). The remaining structural parameters of the intermediate are similar to those for (5,5), but it is 2.3 kcal/mol more stable than the reactant state.

Remarkable for all hydroxo systems is the significantly higher stability of the intermediates in the D reaction step. They are all more stable than the reactants, namely, from (4,OH,1), $\Delta E = −1.1$ kcal/mol, to (4,OH,2), $\Delta E = −3.2$ kcal/mol, to (4,OH,3), $\Delta E = −4.5$ kcal/mol, to (4,OH,4), $\Delta E = −4.7$ kcal/mol, and finally to (4,OH,5), $\Delta E = −2.3$ kcal/mol. The trend is exactly the same for the hexa-aqua systems, and the increase for (4,OH,5) can be accounted for in the same way. A comparison is given in Figure 6. The higher stability of the intermediates results in a higher activation barrier for the back reaction to complete the water exchange cycle. This accounts for the fact that such intermediates have an appreciable lifetime.

Furthermore, the volumes of activation, approximated by $\Delta\Sigma r(Al−O)$, increase in the same way, going from 0.75 to 0.86 to 1.13 Å (Table 3). Therefore, for up to three additional
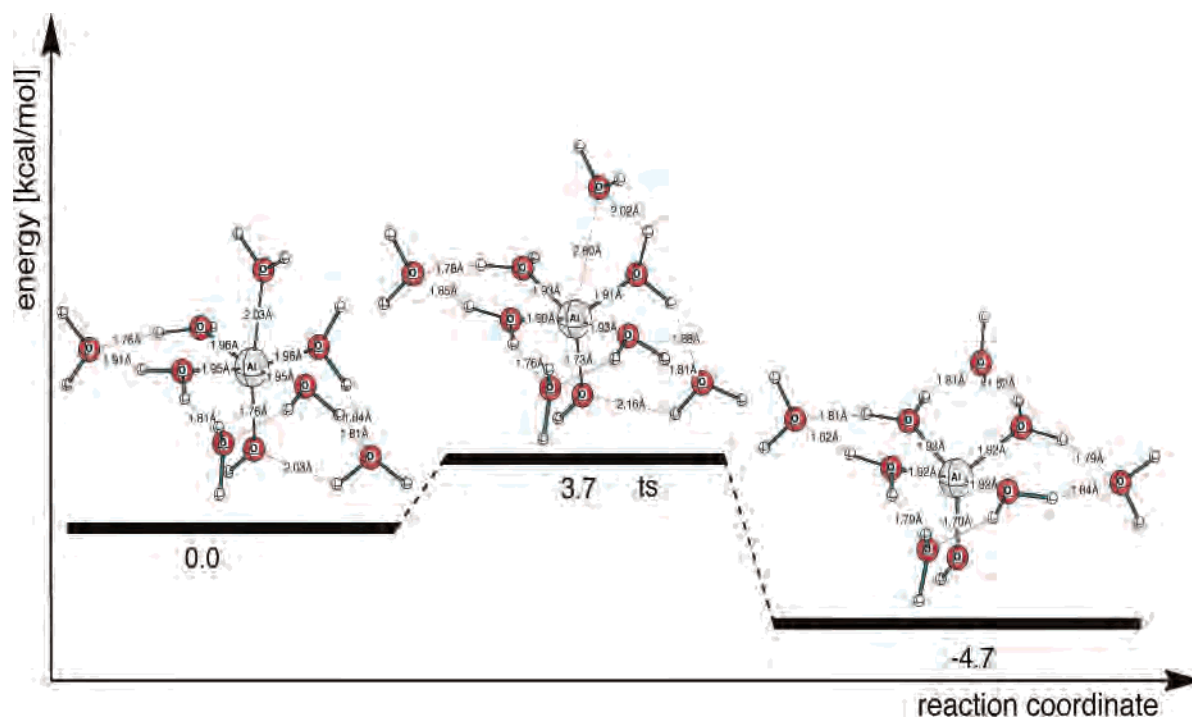
Figure 5. Calculated (B3LYP/6-311+G**) energy profile and selected bond lengths for water exchange on [Al(H$_2$O)$_5$(OH)]$^{2+}$ with explicit consideration of four additional water molecules.
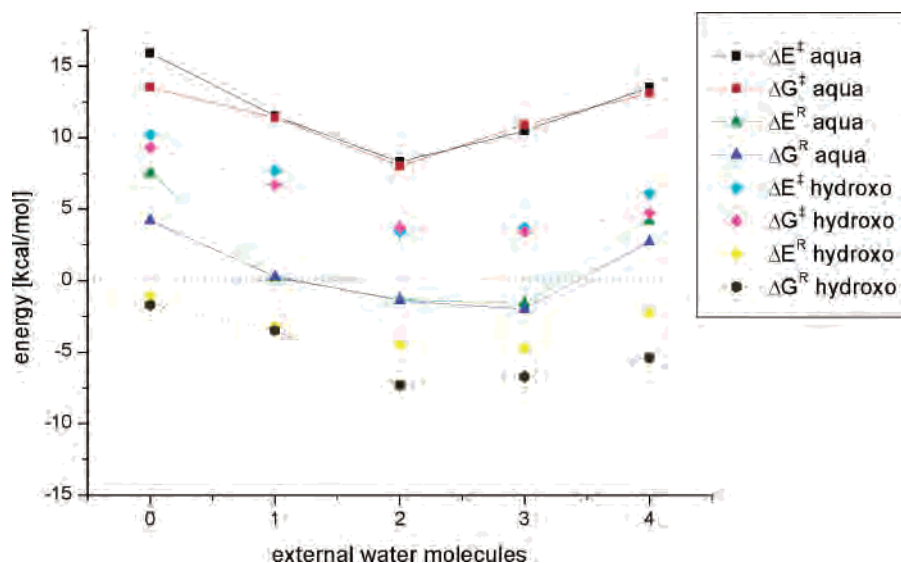

Figure 6. Dependence of the energy of activation and reaction energy on the number of external water molecules.

water molecules, the D character significantly increases, and using these values as criterion, we find that the mechanism is much more D than for the corresponding hexa-aqua systems. Considering three to four water molecules reverses the trend, we find that this can be attributed to the structural distinctions in the (5,OH,4)‡ and (5,OH,5)‡ structures, that is, the external water fixed by three H-bonds, which is not the case for the hexa-aqua systems.

Conclusions

In this study, we have investigated the possible water exchange pathways for the [Al(H$_2$O)$_6$]$^{3+}$ and [Al(H$_2$O)$_5$-(OH)]$^{2+}$ complexes. For the first time, an augmented approach to the standard cluster model of water exchange

processes of Al(III) was used. With respect to the quite slow water exchange process of Al(III), because of the long simulation time necessary to observe an exchange event, accurate dynamic methods are not available up to now. Detailed structural insight is presented as a first step to bridge the gap between considering at least the necessary number of water molecules in the first coordination sphere (cluster model) and a complete second (or higher) coordination sphere.

No transition states and/or intermediates for an A or an I process could be found. We were successful in calculating stationary points on the hypersurface for the D reaction pathway. The energy of activation for the (5,OH) complex is much lower than that for the (6,0) one, namely, 10.2 versus

15.9 kcal/mol. The influence of a solvent sphere on the water exchange process was approximated by considering up to four external water molecules explicitly in the calculations. Even for an incomplete solvent sphere, we found a stabilizing effect of the additional solvent molecules for the D exchange process for all systems. By taking up to two water molecules into account, we found a strong decrease in E_A from 15.9 (6,0) to 8.3 kcal/mol (6,2) for the hexa-aqua complex and from 10.2 (5,OH) to only 3.4 kcal/mol (5,OH,2) for the monohydroxo complex. The increase in E_A on considering three or four water molecules, but still lower than without additional water molecules, shows the important influence of the H-bond network around and within the complexes on the exchange process, however, without changing the nature of the exchange mechanism itself. Without exception, lower activation barriers for the monohydroxo systems, as compared to those of the corresponding hexa-aqua systems, confirm the experimentally known higher exchange rate ($\sim 10^4$ times) of aquated Al(III) at higher pH (>3.0). In addition, the $\Delta\sum r(\text{Al}-\text{O}_{I/II})$ values, which are positive for all of the hexa-aqua and monohydroxo systems studied, not only favor a D reaction mode but also favor a much more D character for the exchange mechanism of the hydroxo complex. Such a behavior is known for all experimentally studied water exchange reactions of aquated metal ions[22-24] and therefore confirms that our model system can describe such exchange processes accurately. Thus, we can convincingly suggest a limiting D water exchange mechanism for $[\text{Al}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$.

Upon comparing the calculated energies of activation with the experimental $\Delta H^{\ddagger}$ values, we found too low energies for the (6,0) system, namely, 15.9 kcal/mol (calculated) compared to 20.2 kcal/mol (experimental), but we found very good agreement for the (5,OH) complex, namely, 10.2 kcal/mol (calculated) compared to 9.9 kcal/mol (experimental). Using the mean values of all reactions studied, we find that 11.9 kcal/mol (hexa-aqua complex) and 6.2 kcal/mol (monohydroxo complex) confirm the experimental trend that the activation barrier for the monohydroxo system is about half that of the hexa-aqua system but agrees less well with the experimental values. As already discussed, we attribute this to the incomplete solvation sphere which should affect the dissociation of a water ligand from the complex to the solvent because of a contribution from the interaction with the H-bond network around the complexes.

Within our selected model system, we see evidence for stable, five-coordinate aquated Al(III) species for both the hexa-aqua and the monohydroxo systems, especially upon taking additional solvent molecules into account. Up to three additional water molecules increase the stability of the intermediates step by step. A single external water molecule in (6,1) stabilizes the intermediate by 7.3 kcal/mol so that the reactant and intermediate are of the same energy. For the (6,2) and (6,3) systems, the intermediates are 1.3 and 1.6 kcal/mol more stable than the reactants. However, much more significant is the fact that all hydroxo intermediates are lower in energy than the reactants, even without external water molecules, for example, (4,OH,1) = -1.7 kcal/mol going to -4.7 kcal/mol for (4,OH,4). Taking thermal corrections into account, that is, to consider $\Delta G^{\ddagger}$ instead of E_A, confirms the results in two ways: first, the general trend for the activation barrier is the same, and second, the hydroxo intermediates are found to be more stable (see Figure 6). Our results, therefore, present strong evidence in favor of the formation of stable, five-coordinate aquated Al(III) species. On the basis of our results, $[\text{Al}(\text{H}_2\text{O})_4(\text{OH})]^{2+}$ is the most stable complex formed by aquated Al(III) in diluted, weakly acidic, aqueous solutions, which provides further support to the recent claims made in the literature.[7]

Supporting Information Available: Calculated energy profiles and selected bond lengths. This material is available free of charge via the Internet at http://pubs.acs.org.

IC061284C