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The water exchange mechanism in thorium (IV) hydrates as studied by quantum chemical methods

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Abstract

The water exchange mechanisms in $[Th(H_2O)_{10}]^{4+}$ and $[Th(H_2O)_9]^{4+}$ along dissociative (D), associative (A) and interchange (I) pathways have been investigated using the ab initio quantum mechanical calculations. Water exchange in $[Th(H_2O)_{10}]^{4+}$ probably proceeds via the D mechanism, the activation energy is 3.06 kcal/mol. The water exchange in $[Th(H_2O)_9]^{4+}$ probably proceeds via the A pathway, the activation energy is 3.62 kcal/mol. Deprotonation of one coordinated water molecule of $[Th(H_2O)_{10}]^{4+}$ leads to the formation of hydroxo-aquo complex $[Th(OH)(H_2O)_9]^{3+}$, which has a more dissociative mechanism and lower activation energy.

Keywords: Water exchange; Quantum chemical calculation; Thorium (IV) hydrates

1. Introduction

Because of high charge and small radius, thorium (IV) has a strong tendency toward hydration. The primary hydration number of Th^{4+} ion is 9–11 based on experimental measurements [1] and 9–10 based on theoretical calculations [2]. The first experimental investigation on the water exchange mechanism of Th^{4+} ion has been made by Farkas et al. [3]. They proposed a dissociative interchange (I_d) mechanism for $[Th(H_2O)_{10}]^{4+}$, but no experimental kinetic parameters such as $\Delta H^{\ddagger}$ or $\Delta S^{\ddagger}$ for the water exchange of Th^{4+}(aq) were available except the minimum water exchange rate $k_{ex} > 5 \times 10^7\ s^{-1}$. The present study focuses on investigating the water exchange mechanisms of thorium (IV) hydrates using the ab initio quantum chemical calculations. We calculated the water exchange mechanisms in $[Th(H_2O)_{10}]^{4+}$ and $[Th(H_2O)_9]^{4+}$. The labilization effect by a hydroxo ligand (OH^-) on the water exchange of Th^{4+} ion was discussed. This is the first computational study on the water exchange in tetravalent actinide ions.

2. Computational methods and reaction model

All the calculations were performed using the Gaussian98 program [4]. The computations of water exchange in $[Th(H_2O)_{10}]^{4+}$ and $[Th(OH)(H_2O)_9]^{3+}$ were performed under the B3LYP hybrid density functional theory [5,6]. The computations of water exchange in $[Th(H_2O)_9]^{4+}$ were made under the HF/MP2 level of theory, where the geometry optimizations were calculated at the HF level and the energy was calculated at the MP2 level. The feasibility of the quantum chemical approximation at the HF/MP2 level was proven elsewhere [7]. The Stuttgart relativistic large core effective core potential (RECP) [8] and the corresponding basis sets were used for thorium, and the 6–31G* basis sets were used for oxygen and hydrogen [9]. The solvent effects were described using the polarized continuum model (PCM) [10] as implemented in Gaussian98. In the PCM model, the solute molecules are embedded in cavities of molecular shape surrounded by a continuous dielectric medium, whose polarization is reproduced by point charges distributed on the cavity surface [10]. Cosentino et al. [11] made a thorough discussion on the inclusion of the bulk solvent effects by the PCM model on aquo-ions of heavy metals. Among all the continuum methods, the PCM model offers a balanced and theoretically sound treatment of all solute–solvent

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interactions at a very reasonable computational cost. The energetics of complex systems can be appropriately calculated in vacuo optimized structures because the term due to the geometry relaxation in solution is not significant. The PCM model has been proven to correctly include the solvation energy of thorium (IV) hydrates in our previous work [2].

For water exchange in $[Th(H_2O)_{10}]^{4+}$ and $[Th(OH)(H_2O)_9]^{3+}$ computed at the B3LYP level, the quantum chemically computed activation energies ($\Delta E^{\ddagger}$) correspond to the Gibbs free energy change ($\Delta G^{\ddagger}_{298}$) where the PCM solvation energy, the zero point energy (ZPE) correction, the thermal correction and the entropy effect [2,12] calculations were made to the electronic energy. For water exchange in $[Th(H_2O)_9]^{4+}$ calculated at the HF/MP2 level, the activation energies ($\Delta E^{\ddagger}$) correspond to the electronic energy at the MP2 level with the inclusion of PCM energy.

The procedures used to investigate the exchange mechanisms follow the path set by Rotzinger et al. [13–16] on *d*-transition and main-group elements. The transition states were identified by a single imaginary frequency corresponding to the substitution of the leaving/entering water. Technically, the transition states were located by stretching or shortening the selected Th–O bond from the ground state configuration of the reactants or from the intermediates. This selected Th–O bond was kept fixed while all the other internal coordinates were optimized until an imaginary substitution mode was found. All the reactants and products/intermediates have no imaginary frequency.

It is not possible to include a complete second coordination sphere in the models, therefore a single water molecule is restricted in the second coordination sphere in the model reactions.

The water exchange in $[Th(H_2O)_{10}]^{4+}$ via the dissociative (*D*), interchange (*I*), and associative (*A*) mechanisms were investigated on the basis of Eqs. (1)–(3), respectively. All the transition states are marked with a superscript pound sign (#).

$$[Th(H_2O)_{10}]^{4+} \rightarrow \{[Th(H_2O)_9 \cdots H_2O]^{4+}\}^{\#} \rightarrow [Th(H_2O)_9]^{4+} \cdot H_2O, \quad (1)$$

$$[Th(H_2O)_{10}]^{4+} \cdot H_2O \rightarrow \{[Th(H_2O)_9 \cdots (H_2O)_2]^{4+}\}^{\#}, \quad (2)$$

$$[Th(H_2O)_{10}]^{4+} \cdot H_2O \rightarrow \{[Th(H_2O)_{10} \cdots H_2O]^{4+}\}^{\#} \rightarrow [Th(H_2O)_{11}]^{4+}. \quad (3)$$

In order to investigate the effect of hydroxyl (OH^-) on the water exchange of $[Th(H_2O)_{10}]^{4+}$, the water exchange in the hydroxo-aquo complex $[Th(OH)(H_2O)_9]^{3+}$ via the *D* mechanism is computed. The computation is based on the following equation:

$$[Th(OH)(H_2O)_9]^{3+} \rightarrow \{[Th(OH)(H_2O)_8 \cdots H_2O]^{3+}\}^{\#} \rightarrow [Th(OH)(H_2O)_8]^{3+} \cdot H_2O. \quad (4)$$

The water exchange in $[Th(H_2O)_9]^{4+}$ via the *A*, *D*, and *I* mechanisms were investigated based on the following equations:

$$[Th(H_2O)_9]^{4+} \cdot H_2O \rightarrow \{[Th(H_2O)_9 \cdots H_2O]^{4+}\}^{\#} \rightarrow [Th(H_2O)_{10}]^{4+}, \quad (5)$$

$$[Th(H_2O)_9]^{4+} \rightarrow \{[Th(H_2O)_8 \cdots H_2O]^{4+}\}^{\#} \rightarrow [Th(H_2O)_8]^{4+} \cdot H_2O, \quad (6)$$

$$[Th(H_2O)_9]^{4+} \cdot H_2O \rightarrow \{[Th(H_2O)_8 \cdots (H_2O)_2]^{4+}\}^{\#}. \quad (7)$$

The geometry of the reactants, products, and transition states were fully optimized in the gas phase without symmetry constraints. The preferred reaction mechanism has the lowest activation energy. The change of the sum of all Th–O bond lengths $\Delta\Sigma d$ (Th–O) occurring during the activation were compared with the volumes of activation ($\Delta V^{\ddagger}$). On the basis of the structure and imaginary mode of the transition states, the $\Delta\Sigma d$ (Th–O) and the activation energies ($\Delta E^{\ddagger}$), the water exchange mechanisms were determined.

3. Results and discussion

3.1. *Water exchange in $[Th(H_2O)_{10}]^{4+}$ via dissociative exchange mechanism*

The calculations were performed on the basis of Eq. (1). All the Th–O bond lengths between thorium and water molecules and the sum of the Th–O bond lengths Σd (Th–O) are given in Table 1. The total energies, activation energies $\Delta E^{\ddagger}$ and the change of the sum of the Th–O bond lengths $\Delta\Sigma d$ (Th–O) which occurred during the water exchange process (Eq. (1)) are reported in Table 2. In the transition state $\{[Th(H_2O)_9 \cdots H_2O]^{4+}\}^{\#}$, the bond length between thorium and the leaving water molecule is 3.404 Å (Fig. 1). In the intermediate $[Th(H_2O)_9]^{4+} \cdot H_2O$, the leaving water molecule situates in the second coordination sphere, and the distance between thorium and the leaving water is 4.249 Å. The transition state and the intermediate $[Th(H_2O)_9]^{4+} \cdot H_2O$ both have approximately C_{2v} symmetry. The reactant has D_{4d} symmetry. The $\Delta E^{\ddagger}$ and $\Delta\Sigma d$ (Th–O) for the *D*-mechanism exchange pathway are 3.06 kcal/mol and 0.351 Å, respectively.

Table 1
Calculated bond lengths (Å) for the species participating in the water exchange reactions in $[Th(H_2O)_{10}]^{4+}$ and $[Th(OH)(H_2O)_9]^{3+}$ at the B3LYP level of theory

Chemical species	D (Th–O)	Σd (Th–O)
$[Th(H_2O)_{10}]^{4+}$ (reactant)	2.684, 2.543, 2.588, 2.543, 2.588, 2.684, 2.543, 2.588, 2.543, 2.588	25.892
$\{[Th(H_2O)_9\cdots(H_2O)]^{4+}\}^{\#}$ (*D*)	2.559, 2.557, 2.572, 2.557, 2.572, 2.462, 2.549, 2.462, 2.549, 3.404	26.243
$[Th(H_2O)_9]^{4+}\cdot H_2O$ (*D*-intermediate)	2.549, 2.590, 2.539, 2.590, 2.539, 2.474, 2.554, 2.474, 2.554, 4.249	27.112
$[Th(H_2O)_{10}]^{4+}\cdot H_2O$ (reactant)	2.584, 2.568, 2.567, 2.578, 2.588, 2.588, 2.580, 2.571, 2.658, 2.507, 4.432	30.220
$\{[Th(H_2O)_{10}\cdots(H_2O)]^{4+}\}^{\#}$ (*A*)	2.613, 2.586, 2.485, 2.648, 2.563, 2.603, 2.620, 2.578, 2.670, 2.456, 3.520	29.342
$[Th(OH)(H_2O)_9]^{3+}$ (reactant)	2.693, 2.082, 2.642, 2.607, 2.647, 2.653, 2.684, 2.684, 2.629, 2.640	25.961
$\{$*trans*-$[Th(OH)(H_2O)_8\cdots(H_2O)]^{3+}\}^{\#}$ (*D*)	2.656, 2.078, 2.616, 2.627, 2.591, 2.516, 2.607, 2.566, 2.623, 3.610	26.490
[*trans*-$Th(OH)(H_2O)_8]^{3+}\cdot H_2O$ (*D* intermediate)	2.631, 2.078, 2.592, 2.648, 2.577, 2.527, 2.611, 2.587, 2.644, 4.338	27.233
$\{$*cis*-$[Th(OH)(H_2O)_8\cdots(H_2O)]^{3+}\}^{\#}$ (*D*)	2.541, 2.078, 2.579, 2.662, 2.637, 2.611, 2.578, 2.587, 2.653, 3.586	26.512
[*cis*-$Th(OH)(H_2O)_8]^{3+}\cdot H_2O$ (*D* intermediate)	2.563, 2.705, 2.556, 2.652, 2.580, 2.607, 2.583, 2.612, 2.682, 4.361	27.900

Table 2
Calculated energies and changes of the sum of the Th–O bond lengths $\Delta\Sigma d$ (Th–O) involved in the water exchange reactions in $[Th(H_2O)_{10}]^{4+}$ and $[Th(OH)(H_2O)_9]^{3+}$ at the B3LYP level of theory

Chemical species	E(SCF)[a] (Hartree)	$G^{\ddagger}$ (298 K)[b] (Hartree)	PCM energy (kcal/mol)	$\Delta E^{\ddagger}$ (kcal/mol)	$\Delta\Sigma d$ (Th-O) (Å)
$[Th(H_2O)_{10}]^{4+}$ (reactant)	−798.837824	−798.664171	−647.96	0	0
$\{[Th(H_2O)_9\cdots(H_2O)]^{4+}\}^{\#}$ (*D*)	−798.846078	−798.670989	−640.62	3.06	0.351
$[Th(H_2O)_9]^{4+}\cdot H_2O$ (*D* intermediate)	−798.861858	−798.688219	−631.19	1.68	1.220
$[Th(H_2O)_{10}]^{4+}\cdot H_2O$ (reactant)	−875.323206	−875.102979	−621.58	0	0
$\{[Th(H_2O)_{10}\cdots(H_2O)]^{4+}\}^{\#}$ (*A*)	−875.298906	−875.078806	−631.48	5.27	−0.878
$[Th(OH)(H_2O)_9]^{3+}$ (reactant)	−798.865135	−798.704729	−369.53	0	0
$\{$*trans*-$[Th(OH)(H_2O)_8\cdots(H_2O)]^{3+}\}^{\#}$ (*D*)	−798.874042	−798.711099	−363.26	2.27	0.529
[*trans*-$Th(OH)(H_2O)_8]^{3+}\cdot H_2O$ (*D* intermediate)	−798.884170	−798.722664	−359.00	0.72	1.272
$\{$*cis*-$[Th(OH)(H_2O)_8\cdots(H_2O)]^{3+}\}^{\#}$ (*D*)	−798.871782	−798.707165	−364.46	3.54	0.551
[*cis*-$Th(OH)(H_2O)_8]^{3+}\cdot H_2O$ (*D* intermediate)	−798.883792	−798.723017	−359.76	1.71	1.939

[a] SCF energy in gas phase at 0 K, 0 atm.

[b] Net free energy after adjustment for the concentration in liquid ($p = 1354$ atm), the ZPE correction and thermal correction are included.

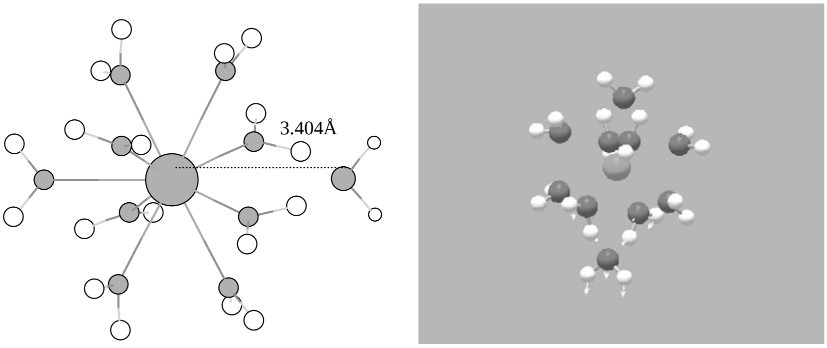

Fig. 1. Water exchange in $[Th(H_2O)_{10}]^{4+}$ via the *D* mechanism. Perspective view (left) and the imaginary mode (right) of the transition state of $\{[Th(H_2O)_9\cdots H_2O]^{4+}\}^{\#}$ with C_{2v} symmetry.

The lifetime (τ) of the intermediate $[Th(H_2O)_9]^{4+}\cdot H_2O$ formed in the *D*-mechanism pathway is calculated based on the following equations:

$$[Th(H_2O)_9]^{4+}\cdot H_2O(\text{intermediate}) \rightarrow \{[Th(H_2O)_9\cdots H_2O]^{4+}\}^{\#}(\text{transition state}), \quad (8)$$

$$\tau = 1/k, \quad k = Z\exp\{-\Delta E_{\mathrm{I}}^{\ddagger}/RT\}, \quad (9)$$

where $Z \approx 10^{11}\,\mathrm{s}^{-1}$. The activation energy $\Delta E_I^{\ddagger}$ of this reaction is 1.38 kcal/mol. The lifetime τ of the intermediate $[Th(H_2O)_9]^{4+}\cdot H_2O$ is 0.102 ns.

3.2. Water exchange in $[Th(H_2O)_{10}]^{4+}$ via associative exchange mechanism

The calculations were performed on the basis of Eq. (3). The transition state $\{[Th(H_2O)_{10}\cdots H_2O]^{4+}\}^{\#}$ is

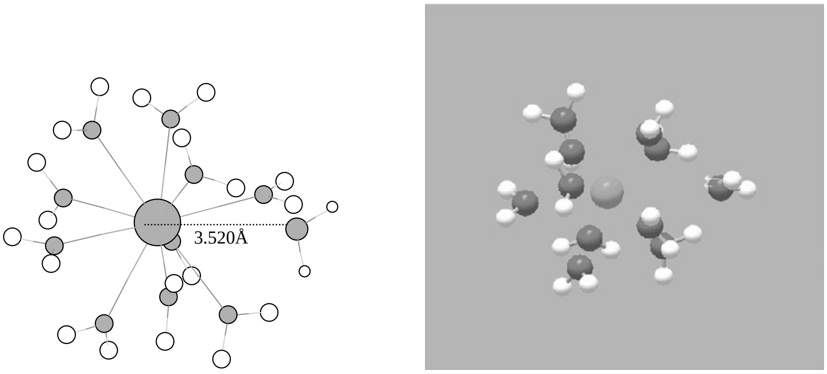

Fig. 2. Water exchange in $[Th(H_2O)_{10}]^{4+}$ via the *A* mechanism. Perspective view (left) and the imaginary mode (right) of the transition state $\{[Th(H_2O)_{10}\cdots H_2O]^{4+}\}^{\#}$ with C_1 symmetry.

located at the Th–O bond distance of 3.520 Å (Fig. 2). The structure parameters are given in Table 1. The activation energy $\Delta E^{\ddagger}$ and the change of the sum of Th–O bond lengths $\Delta\Sigma d$ (Th–O) are 5.27 kcal/mol and −0.878 Å, respectively (Table 2). In this reaction sequence, the imaginary vibrational frequency of the transition state describes the motion of the activated ligand toward the first coordination sphere.

The activation energy $\Delta E^{\ddagger}$ via the *A* mechanism is 2.21 kcal/mol larger than that via the *D* mechanism, which demonstrates that water exchange in $[Th(H_2O)_9]^{4+}$ is favorable to proceed via the *D* mechanism than via the *A* mechanism.

Computations on the *I* mechanism based on Eq. (2) were also investigated, but the attempts to identify the proper transition state $\{[Th(H_2O)_9\cdots(H_2O)_2]^{4+}\}^{\#}$ with only one imaginary vibrational frequency failed. Only the saddle points with two imaginary frequencies could be found. The distinction of *D* and I_d mechanisms is not possible in the present calculations. Rotzinger [16] found no transition state of the I_d mechanism for all thus-far-investigated hexaaqua ions and the reason was due to the omission of the second coordination sphere, H–bonding of the exchanging H_2O ligands with equatorial aqua ligand is favored over the weak M–OH_2 bonds. If these H–bonds are formed by H_2O molecules of the second coordination sphere, structures with weak M–H_2O bonds might be obtained. For the present calculated model $[Th(H_2O)_{10}]^{4+}$, if a complete second hydration shell is added explicitly, at least 30 H_2O molecules would be involved. It is too large and difficult for practical implementation at the present computational cost. Thus, when computations are performed for a dissociative activation in the gas phase model or the model being used for the present work where the second hydration shell and bulk water are represented by a dielectric continuum, only structures for the *D* pathway could be obtained. This result should not be taken as evidence against the existence of the I_d mechanism.

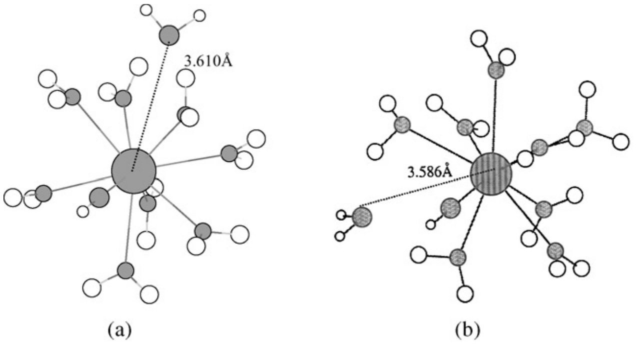

Fig. 3. Water exchange in $[Th(OH)(H_2O)_9]^{3+}$ via the *D* mechanism. Perspective view of the transition states (a) $\{trans\text{-}[Th(OH)(H_2O)_8\cdots\nsucc H_2O]^{3+}\}^{\#}$ with C_1 symmetry; and (b) $\{cis\text{-}[Th(OH)(H_2O)_8\cdots H_2O]^{3+}\}^{\#}$ with C_1 symmetry.

Calculated results show that the water exchange in $[Th(H_2O)_{10}]^{4+}$ proceeds via the *D* or I_d mechanism. In order to investigate the effect of hydroxyl ligand (OH^-) on the water exchange in $[Th(H_2O)_{10}]^{4+}$, water exchange in its hydroxo-aquo complex $[Th(OH)(H_2O)_9]^{3+}$ via the *D* mechanism was further computed.

3.3. Water exchange in $[Th(OH)(H_2O)_9]^{3+}$ via dissociative exchange mechanism

The calculations were performed on the basis of Eq. (4). The leaving water molecule opposite to hydroxyl ligand (OH^-) leads to the transition state $\{[trans\text{-}Th(OH)(H_2O)_8\cdots H_2O]^{3+}\}^{\#}$ (Fig. 3). The dissociation of the transition state leads to the intermediate $[trans\text{-}Th(OH)(H_2O)_8]^{3+}\cdot H_2O$. All the reactant, the transition state, and the intermediate have C_1 symmetry. The bond lengths between thorium and water molecules, and the sum of the Th–O bond lengths Σd (Th–O) are given in Table 1. The activation energies $\Delta E^{\ddagger}$ and the $\Delta\Sigma d$ (Th–O) which occurred during the water exchange process (Eq. (4)) are reported in Table 2. The $\Delta E^{\ddagger}$ and $\Delta\Sigma d$ (Th–O) are 2.22 kcal/mol and 0.529 Å, respectively.

Table 3
Calculated bond lengths (Å) for the species participating in the water exchange reactions in $[Th(H_2O)_9]^{4+}$ at the HF level of theory

Chemical species	*d* (Th–O)	*Σd* (Th–O)
$[Th(H_2O)_9]^{4+}\cdot(H_2O)$ (reactant)	2.577, 2.555, 2.573, 2.575, 2.582, 2.523, 2.460, 2.573, 2.562, 4.383	27.399
$\{[Th(H_2O)_9\cdots(H_2O)]^{4+}\}^{\#}$ (*A*)	2.587, 2.564, 2.593, 2.585, 2.580, 2.507, 2.505, 2.577, 2.557, 3.513	26.568
$[Th(H_2O)_9]^{4+}$(reactant)	2.559, 2.559, 2.559, 2.567, 2.567, 2.567, 2.559, 2.559, 2.559	23.055
$\{[Th(H_2O)_8\cdots(H_2O)]^{4+}\}^{\#}$ (*D*)	2.485, 2.535, 2.527, 2.557, 2.557, 2.485, 2.535, 2.527, 3.490	23.698
$[Th(H_2O)_8]^{4+}\cdot(H_2O)$ (*D* intermediate)	2.482, 2.533, 2.551, 2.533, 2.533, 2.482, 2.532, 2.551, 4.339	24.536

Table 4
Calculated energies and changes of the sum of the Th–O bond lengths $\Delta\Sigma d$ (Th–O) involved in the water exchange reactions in $[Th(H_2O)_9]^{4+}$ at the MP2 level of theory

Chemical species	*E* (MP2)[a] (Hartree)	PCM energy (kcal/mol)	$\Delta E^{\ddagger}$ (kcal/mol)	$\Delta\Sigma d$ (Th–O) (Å)
$[Th(H_2O)_9]^{4+}\cdot(H_2O)$ (reactant)	−796.606572	−627.27	0	0
$\{[Th(H_2O)_9\cdots(H_2O)]^{4+}\}^{\#}$ (*A*)	−796.586864	−636.02	3.62	−0.831
$[Th(H_2O)_9]^{4+}$ (reactant)	−720.338459	−654.01	0	0
$\{[Th(H_2O)_8\cdots(H_2O)]^{4+}\}^{\#}$ (*D*)	−720.323820	−645.12	18.08	0.643
$[Th(H_2O)_8]^{4+}\cdot(H_2O)$ (*D* intermediate)	−720.333101	−641.45	15.92	1.481

[a] MP2 energy in gas phase.

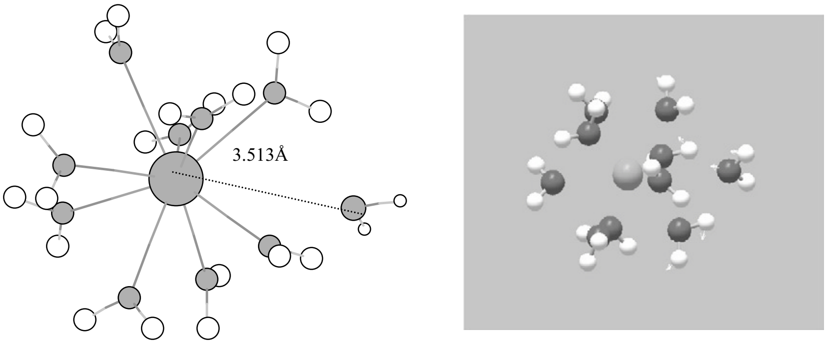

Fig. 4. Water exchange in $[Th(H_2O)_9]^{4+}$ via the *A*-mechanism. Perspective view (left) and the imaginary mode (right) of the transition state $\{[Th(H_2O)_9\cdots H_2O]^{4+}\}^{\#}$ with C_1 symmetry.

The transition state of the leaving water molecule adjacent to hydroxyl (OH^-) $\{[$*cis*-$Th(OH)(H_2O)_8\cdots\nsucc H_2O]^{3+}\}^{\#}$ is identified at the Th–O bond length of 3.586 Å (Fig. 3). The $\Delta E^{\ddagger}$ and $\Delta\Sigma d$ (Th–O) are 3.52 kcal/mol and 0.551 Å, respectively (Table 2). It demonstrates that when $[Th(OH)(H_2O)_9]^{3+}$ proceeds via a *D*-mechanism water exchange, the leaving water opposite to OH^- has lower energy barrier. It is more favorable to operate the *D*-mechanism water exchange when the leaving water and OH^- are in *trans* position than the leaving water and OH^- are in *cis* position.

By comparing the $\Delta E^{\ddagger}$ of water exchange in $[Th(H_2O)_{10}]^{4+}$ with that in $[Th(OH)(H_2O)_9]^{3+}$ via the *D* mechanism, it is found that the $\Delta E^{\ddagger}$ of $[Th(OH)(H_2O)_9]^{3+}$ is 0.90 kcal/mol lower than that of $[Th(H_2O)_{10}]^{4+}$. It indicates that $[Th(OH)(H_2O)_9]^{3+}$ has lower energy barrier than $[Th(H_2O)_{10}]^{4+}$ to proceed via the *D*-mechanism water exchange. The labilization is caused by the deprotonation of a coordinated water molecule. In addition, $[Th(OH)(H_2O)_9]^{3+}$ has 0.178 Å larger $\Delta\Sigma d$ (Th–O) value than $[Th(H_2O)_{10}]^{4+}$. It argues that the labilization by a hydroxo ligand (OH^-) is accompanied by a more dissociative mechanism in $[Th(OH)(H_2O)_9]^{3+}$ than in $[Th(H_2O)_{10}]^{4+}$. The labilization by a hydroxo ligand (OH^-) has also been reported for hexaaqua complexes of Fe(III), Rh(III) and Ir(III) [17,18].

3.4. *Water exchange in $[Th(H_2O)_9]^{4+}$ via associative exchange mechanism*

The computations were performed based on Eq. (5). The calculations were made at the HF/MP2 level of theory because it was difficult to find the proper transition state at the B3LYP level of theory. All the

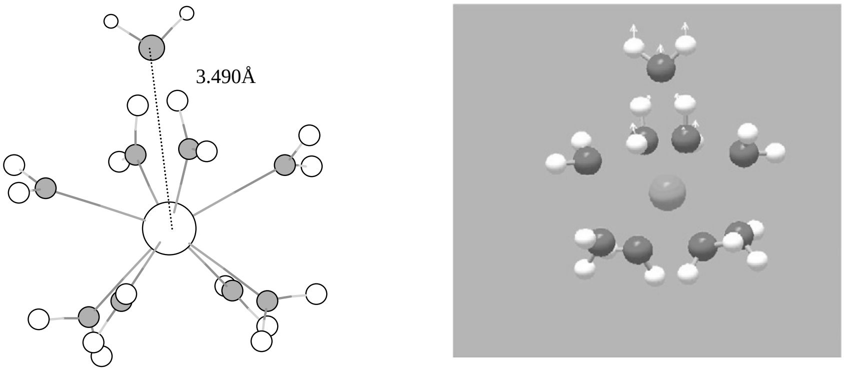

Fig. 5. Water exchange in $[Th(H_2O)_9]^{4+}$ via the D mechanism. Perspective view (left) and the imaginary mode (right) of the transition state $\{[Th(H_2O)_8 \cdots H_2O]^{4+}\}^{\#}$ with C_1 symmetry.

Th–O bond lengths between thorium and water molecules and the sum of the Th–O bond lengths Σd (Th–O) are given in Table 3. The total energies, activation energies $\Delta E^{\ddagger}$ and the change of the sum of the Th–O bond lengths $\Delta\Sigma d$ (Th–O) involved in the water exchange in $[Th(H_2O)_9]^{4+}$ are shown in Table 4. The distance between Th and the entering water in the transition state $\{[Th(H_2O)_9 \cdots (H_2O)]^{4+}\}^{\#}$ is 3.513 Å (Fig. 4). The $\Delta\Sigma d$(Th–O) is −0.831 Å, and the corresponding activation energy $\Delta E^{\ddagger}$ is 3.62 kcal/mol. In this reaction sequence, the imaginary vibrational frequency of the transition state describes the motion of the activated ligand toward the first coordination sphere. The stable intermediate state was not found in the present computation model.

3.5. Water exchange in $[Th(H_2O)_9]^{4+}$ via dissociative exchange mechanism

The computations were performed on the basis of Eq. (6). The transition state $\{[Th(H_2O)_8 \cdots H_2O]^{4+}\}^{\#}$ was identified at the Th–O bond length between Th and the leaving water of 3.490 Å (Fig. 5). The calculated bond lengths are given in Table 3. The total energies, $\Delta E^{\ddagger}$ and $\Delta\Sigma d$ (Th–O) are given in Table 4. The $\Delta\Sigma d$ (Th–O) is 0.643 Å. The $\Delta E^{\ddagger}$ is 18.08 kcal/mol, which is significantly larger than 3.62 kcal/mol of the A mechanism. The water exchange in $[Th(H_2O)_9]^{4+}$ does not likely to proceed via the D mechanism. The water exchange in $[Th(H_2O)_9]^{4+}$ is preferable to an associative pathway.

Water exchange in $[Th(H_2O)_9]^{4+}$ via the interchange exchange mechanism based on Eq. (7) was also computed. One additional water in the second hydration shell acts as a potential ligand that enters into the first hydration shell. Unfortunately, the proper transition state $\{[Th(H_2O)_8 \cdots (H_2O)_2]^{4+}\}^{\#}$ with only one imaginary vibrational frequency indicating the substitution mode of the entering and leaving water could not be located. The saddle points have two imaginary frequencies. In the present computation model, we failed to distinguish the A and I_a mechanisms for $[Th(H_2O)_9]^{4+}$.

4. Conclusions

Based on the structures and the imaginary modes of the transition states, together with the activation energies $\Delta E^{\ddagger}$, the change of the sum of bond length $\Delta\Sigma d$ (Th–O) that occurred during the water exchange reactions, it is found that the water exchange in $[Th(H_2O)_{10}]^{4+}$ probably proceeds via the D mechanism. Due to the labilization by the hydroxo ligand (OH^-), its hydroxo-aquo complex $[Th(OH)(H_2O)_9]^{3+}$ proceeds via a more dissociative mechanism than $[Th(H_2O)_{10}]^{4+}$. The water exchange in $[Th(H_2O)_9]^{4+}$ probably follows the A mechanism.

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