Theoretical Study of the Water Exchange Reaction on Divalent Zinc Ion using Density Functional Theory

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Abstract

Recent *ab initio* studies reported in the literature have challenged the mechanistic assignments made on the basis of volume of activation data [1,2]. In addition to that *ab initio* molecular orbital calculations on hydrated zinc(II)-ions were used to elucidate the general role of this ion in metalloproteins [3]. Due to our interest in both inorganic reaction mechanisms and enzymatic catalysis we started a systematic investigation of solvent exchange processes on divalent zinc-ion using density functional calculations. Our investigations cover aqua complexes of the general form $[Zn(H_2O)_n]^{2+} \cdot mH_2O$ with n=3-6 and m=0-2, where n and m represent the number of water molecules in the coordination and solvation sphere, respectively.

The complexes $[Zn(H_2O)_5]^{2+} \cdot 2H_2O$ and $[Zn(H_2O)_4]^{2+} \cdot 2H_2O$ turnend out to be the most stable zinc complexes with seven and six water molecules, respectively. This implies that a heptacoordinated zinc(II) complex, where all water molecules are located in the co-ordination sphere, should be energetically highly unfavorable and that $[Zn(H_2O)_6]^{2+}$ can quite readily push two coordinated water molecules into the solvation sphere. For the pentaqua complex $[Zn(H_2O)_5]^{2+}$ only one water molecule is easily lost to the solvation sphere, which makes the $[Zn(H2O)_4]^{2+} \cdot H_2O$ complex the most favorable in order to consider the limiting dissociative and associative water exchange process of hexacoordinated zinc(II). The dehydration and hydration energies using the most stable zinc(II) complexes $[Zn(H_2O)_4]^{2+} \cdot 2H_2O$, $[Zn(H_2O)_5]^{2+} \cdot 2H_2O$ and $[Zn(H_2O)_4]^{2+} \cdot H_2O$ were calculated to be 24.1 and -21.0 kcal/mol, respectively.

Keywords: *ab inito*, DFT, zinc complexes, hydration energies

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 and SCF calculations reported in the literature has challenged the mechanistic assignments made on the basis of volume of activation data [1,2]. In addition to that *ab initio* molecular orbital calculations on hydrated Zn^{2+} ions were used to elucidate the general role of this ion in metalloproteins [3]. In this respect, the application of density functional theory

Table 1. *Total molecular energies (au) and zero-point energies (kcal/mol) of [Zn(H₂O)ₙ]²⁺·mH₂O*

n+m [a]	n	m	B3LYP/SHA1 [b]	ZPE [c]	B3LYP/SHA2 [d]	B3LYP/SHA3 [e]
7	6	1	-2313.239 035	107.0	-2314.205 809	-2314.163 070
7	5	2	-2313.250 312	107.3	-2314.215 864	-2314.171 175
6	6	0	-2236.850 392	89.9	-2237.710 038	-2237 672 247
6	5	1	-2236.856 859	91.5	-2237.713 126	-2237.674 948
6	4	2	-2236.862 967	92.4	-2237.716 919	-2237.678 007
5	5	0	-2160.460 229	75.1	-2161.207 801	-2161.175 511
5	4	1	-2160.464 991	76.5	-2161.210 592	-2161.178 306
5	3	2	-2160.443 825	76.8	-2161.189 460	-2161.157 477
H₂O			-76.341 524	13.0	-76.461 570	-76. 456 609
Zn(II)			-1778.187 233		-1778.375 868	-1778.375 868

[a]   n = number of coordinated water molecules,
      m = number of closely associated water molecules in
      the solvation sphere
[b]   B3LYP/SHA1=B3LYP/SHA1//B3LYP/SHA1
[c]   calculated at B3LYP/SHA1//B3LYP/SHA1
[d]   B3LYP/SHA2=B3LYP/SHA2//B3LYP/SHA1
[e]   B3LYP/SHA3 = B3LYP/SHA3//B3LYP/SHA1

(DFT) to transition metal complexes opens new opportunities to describe the hydration of metal ions, as recently shown for the stepwise hydration of Fe^{3+} [4]. Due to our interest in both inorganic reaction mechanisms and enzymatic catalysis we started a systematic investigation of solvent exchange processes on divalent zinc ion using density functional calculations. Our investigations cover aqua complexes of the general form $[Zn(H_2O)_n]^{2+}\cdot mH_2O$ with n=3-6 and m=0-2, where n and m represent the number of water molecules in the coordination and solvation sphere, respectively. First we studied the stepwise hydration of Zn^{2+} ions. In order to include the limiting dissociative and associative substitution modes of the octahedral hexaqua cation, we next focussed on coordination numbers between 5 and 7. Our findings enable us to comment on related results reported in the literature for the hydration of Zn^{2+} ions [1-3] and to emphasize fundamental requirements that must be fulfilled in order to draw mechanistic conclusions from such calculations.

Methods

Calculations were carried out on a CONVEX SPP-1000 computer and on HP-735 PA-RISC workstations at the Computer-Chemie-Centrum Erlangen, using GAUSSIAN 94 [5] and the B3LYP hybrid functional [6,7]. The optimized split

valence basis set of Ahlrichs et al. [8], augmented with p- and d-type polarization functions, was used for geometry optimizations and frequency analyses. The latter procedure verified that all structures presented in this work are indeed local minima with respect to their potential energy surface. The final adopted zinc-basis set was of the form [14s9p5d/5s3p3d], whereas the oxygen contraction pattern was [7s4p1d/3s2p1d]. The hydrogen [4s/2s] set remained unchanged. For convenience, this combined basis set will be further referred to as SHA1. For the refinement of the total energy, single point calculations were performed using two modified double zeta Schäfer-Horn-Ahlrichs basis sets for zinc, oxygen and hydrogen [8]. Both types of combinations have two additional p- and d-type polarization functions for zinc forming a [14s11p5d2f/8s7p3d2f] basis set and two d-type polarization functions for oxygen giving a [10s6p2d/6s3p2d] basis set. However they differ in the hydrogen and oxygen parameter sets. The first combination, referred to as SHA2, includes a p-type polarization function on hydrogen forming a [5s1p/3s1p] basis set, whereas the second parameter set, abbreviated as SHA3, contains a diffuse s function for hydrogen giving a [6s/4s] basis set and an additional diffuse sp function for oxygen.

Results and Discussion

Total molecular energies of all structures of the type $[Zn(H_2O)_n]^{2+}\cdot mH_2O$, where n and m represent the water molecules in the coordination and solvation sphere, respectively, are summarized in Table 1. In the case of heptahydrated zinc(II) ions, the most stable structures, in contrast to those published by another group [1,2], have at least one water molecule in the solvation sphere. Although

(a)

(b)
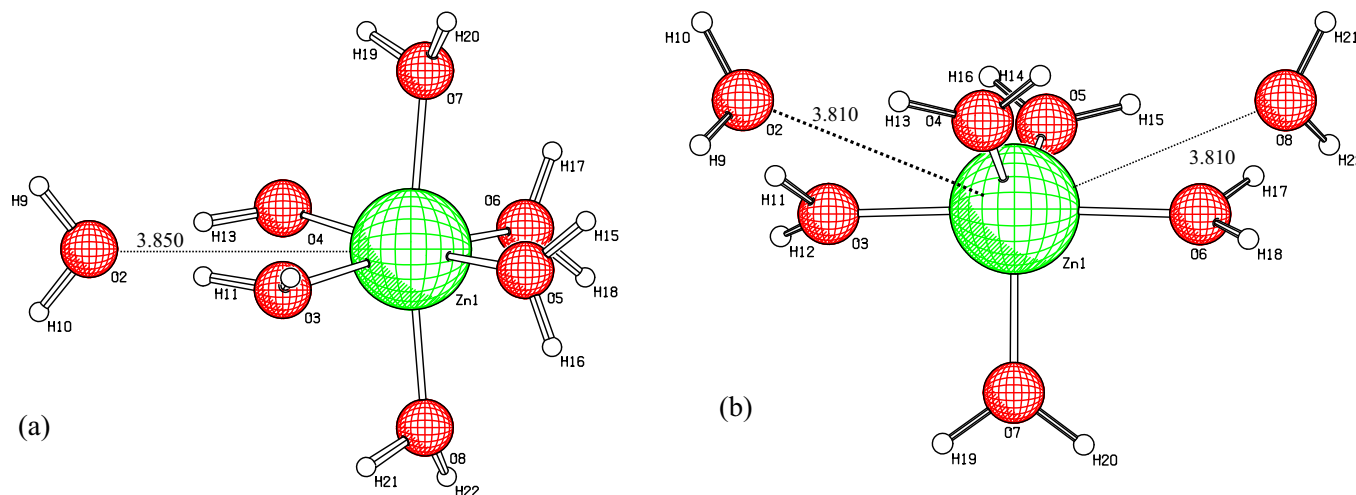
Figure 1. *Molecular geometries from B3LYP/SHA1//B3LYP/ SHA1 calculations. Bond lenghts given in Angstrom. (a) [Zn(H₂O)₆]²⁺·H₂O; PG=C₂.*

(b) [Zn (H₂O)₅]²⁺·2H₂O; PG=C₁

Glusker et al.[3] mentioned this behavior, they did not present any structural data or total energies for heptahydrated Zn^{2+} ions. However, in order to discuss the water exchange behavior of Zn^{2+} ions, these solvent complexes are essential, especially when searching for a suitable transition state structure. Calculations on the B3LYP/ SHA1//B3LYP/SHA1 level show that $[Zn(H_2O)_6]^{2+}\cdot H_2O$ and $[Zn(H_2O)_5]^{2+}\cdot 2H_2O$ are more stable than the corresponding hexaqua complex with one separated water molecule (Figure 1). Taking into account the zero point energy correction (ZPE), these differences were calculated to be 25.5 kcal/mol and 32.3 kcal/mol, respectively, thus

making $[Zn(H_2O)_5]^{2+}\cdot 2H_2O$ the most favourable heptaqua complex in the gas phase. The same trend can be observed when going to the hexaqua complexes, i.e. $[Zn(H_2O)_4]^{2+}\cdot 2H_2O$ is 2.9 kcal/mol more stable than $[Zn(H_2O)_5]^{2+}\cdot H_2O$, and 5.4 kcal/mol lower in energy than $[Zn(H_2O)_6]^{2+}$. This implies that in the gas phase hexaqua Zn^{2+} can push two coordinated water molecules into the solvation sphere. This behavior changes when going to the pentaqua complexes. Here only one water molecule is easily lost to the solvation sphere, which makes the $[Zn(H_2O)_4]^{2+}\cdot H_2O$ complex the most favorable one. The energy difference between this complex and $[Zn(H_2O)_5]^{2+}$ was calculated to be 1.6 kcal/mol, compared to 13.6 kcal/ mol between this complex and $[Zn(H_2O)_3]^{2+}\cdot 2H_2O$.

Inclusion of additional polarization and diffuse functions in the SHA2 and SHA3 basis sets, does not change the above conclusions. The tendency of Zn^{2+} ions with more than four water molecules in the coordination sphere to release their fifth and sixth waters into the solvation sphere

Table 2. *Calculated relative stabilities (kcal/mol) for the movement of water molecules from the coordination sphere into the solvation sphere and hydration energies (kcal/mol) for the reaction of the most stable aqua complexes of the zinc(II)-ion corrected for zero-point energies.*

n+m [a]	(n,m) → (o,p) [b]	B3LYP/SHA1 [a]	B3LYP/SHA2 [a]	B3LYP/SHA3 [a]
7	(6,1) → (5,2)	-6.8	-6.0	-4.8
6	(6,0) → (5,1)	-2.5	-0.3	-0.1
6	(5,1) → (4,2)	-2.9	-1.5	-1.0
5	(5,0) → (4,1)	-1.6	-0.4	-0.4
5	(4,1) → (3,2)	13.6	13.6	13.4
6 +H₂O	(4,2) +H₂O → (5,2)	-26.9	-21.6	-21.0
6 - H₂O	(4,2) - H₂O → (4,1)	32.5	25.2	24.1

[a] *see footnote to Table1*

[b] *(n,m)=[Zn(H₂O)ₙ]²⁺·mH₂O, (o,p) = [Zn(H₂O)ₒ]²⁺·pH₂O*

is maintained. The calculated energies are in good agreement with those published by Glusker et al.[3]. However, the trend of releasing water molecules into the solvation sphere is more pronounced and is most conspicuous when dealing with the heptaqua Zn^+ ions. Here the energy difference between the most stable complex $[Zn(H_2O)_5]^{2+}\cdot 2H_2O$ and $[Zn(H_2O)_6]^{2+}\cdot H_2O$ on the B3LYP/SHA3//B3LYP/SHA1 level is approximately 5 times higher than the analogous difference between $[Zn(H_2O)_5]^{2+}\cdot H_2O$ and $[Zn(H_2O)_4]^{2+}\cdot 2H_2O$ and even 50 times higher than the energy difference between $[Zn(H_2O)_6]^{2}$ and $[Zn(H_2O)_5]^{2+}\cdot H_2O$ (Table 2). This, however, indicates that a heptacoordinated zinc(II) complex, where all water molecules are located in the coordination sphere, should be energetically highly unfavorable. Thus a mechanistic assignment based only on the complexes $[Zn(H_2O)_7]^{2+}$, $[Zn(H_2O)_6]^{2+}$ and $[Zn(H_2O)_5]^{2+}$ as used by others [1,2] should be considered with care.

In order to cover the limiting associative and dissociative water exchange processes of hexacoordinated Zn^{2+} and to calculate energies for hydration and dehydration, respectively, it is necessary to consider the most stable gas phase complexes obtained by the DFT calculations. Scheme 1 shows the reaction of the most stable hexacoordinated zinc(II) complex $[Zn(H_2O)_4]^{2+}\cdot 2H_2O$ with water, yielding the most stable heptacoordinated aqua species $[Zn(H_2O)_5]^{2+}\cdot 2H_2O$. In the same way, the dissociation of water results in a pentaqua complex which is best described as $[Zn(H_2O)_4]^{2+}\cdot H_2O$.

$$[Zn(H_2O)_4]^{2+}\cdot 2H_2O + H_2O \quad \rightarrow \quad [Zn(H_2O)_5]^{2+}\cdot 2H_2O$$

$$[Zn(H_2O)_4]^{2+}\cdot H_2O + H_2O \quad \rightarrow \quad [Zn(H_2O)_4]^{2+}\cdot 2H_2O$$
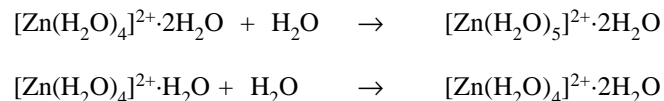
Scheme 1

The energies for the stepwise release of water molecules from the coordination sphere into the solvation sphere and the reaction energies for the hydration and dissociation of water, respectively, are also included in Table 2.

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