Density functional theory calculations for the microsolvation of $M^{3+}$–zwitterionic glycine complexes ($M^{3+} = Al^{3+}, Ga^{3+}, In^{3+}$)

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1. Introduction

An understanding of the interaction between metal ions and amino acids is essential to the elucidation and interpretation of a large number of fundamental biological processes, such as the reversible dioxygen binding and activation, electron transfer, or oxidation. These processes often involve the complexation of metal ions with amino acid residues of proteins, which determine the structure, function, and activity of the metalloproteins [1]. Aluminum, a ubiquitous metal, is expected to form a huge variety of stable complexes with diverse biofunctional ligands [2] such as transferrin protein, sulfur-containing amino acid chains and aromatic amino acid. The binding of $Al^{3+}$ ion to these bioligands dramatically alters their structures and chemical properties. For a number of metalloproteins, the incorporated $Al^{3+}$ ion can substitute other metal ions and permanently occupy the active binding sites, which strongly affect the functions and performance of the metalloproteins [1,3,4]. For example, the $Al^{3+}/Mg^{2+}$ exchange in $Mg^{2+}$-based metalloproteins gives rise to the inefficient performance of the metalloproteins [1,4]. Therefore, $Al^{3+}$ ion can play an essential role in the biological systems.

The simplest and smallest amino acid, glycine (Gly), found in proteins has been used extensively as a model compound for theoretical and experimental studies aiming at the elucidation of the interaction existing between metal ions and biological systems in many life processes. Naturally occurring Gly amino acid exhibits the zwitterionic structures in the solid state and in aqueous solution with a wide pH range, whereas in the gas phase it has the neutral form [5–12]. Theoretical calculations and experimental observations established the Gly zwitterions in the isolated state are not even local minima on the potential energy surface (PES) and can transit into the neutral structures with no energy barrier. The presence of metal ions can result in the stabilization of the zwitterionic Gly (GlyZwitt.) [13–18]. It is found that the monovalent metal ions generally yield the local energy minima on the PES for metal-GlyZwitt. Complexes [13–15], while most of the divalent metal ions can render the global minima [15–18].

Recently, a variety of investigations have been devoted to the exploration of microhydration of amino acids and metal-amino acid complexes [19–27]. It is of particular importance to conduct such studies, as the majority of biological processes take place in aqueous environments and most biochemical reactions take place within the first hydration shell. For the hydration of both Gly,$M^{n+}$ and GlyZwitt.$M^{n+}$ ($M = Li, Na, K, Mg, Ca, Ni, Cu and Zn, n = 1$ or $2$) complexes, the addition of two or five water molecules results in a net preference of non-zwitterionic complexes with the exception for $M = K$ system which has a net preference of GlyZwitt.$K^{+}[(H_2O)_5]$ complex [24]. For the hydration of the complexed structures of Gly with the first row transition-metal ions ($Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}$), the addition of solvation sphere gives rise to an octahedral arrangement around $Ni^{2+}, Co^{2+}$, and $Fe^{2+}$ ions, bipyramidal-trigonal geometry for $Mn^{2+}$ and $Zn^{2+}$, and square-pyramidal geometry around $Cu^{2+}$ ion [25].

In this Letter, we perform first-principles calculations using density functional theory to study the incremental hydration of GlyZwitt.$M^{3+}$ complexes ($M^{3+} = Al^{3+}, Ga^{3+}, In^{3+}$). The Gly biomolecule is found to behave as a mono- or bidentate ligand and exhibit the zwitterionic form, which is in contrast with the non-zwitterionic Gly ligand in the hydrated complexes of divalent ions with...
Gly. The strong electrostatic interaction between the hydrated trivalent M$^{3+}$ ions and Gly is expected to stabilize the Gly zwitierons. The water molecule ligand is added stepwise to GlyZwitt.M$^{3+}$ complexes. The first solvation shell around the metal ions is found to emerge in GlyZwitt.M$^{3+}$(H$_2$O)$_5$ complexes, which exhibit the hexacoordinate configuration around the metal center. Further added water molecule is transferred to the outer hydration shell, where the hydrogen bond is formed. In the previous investigations on the hydration of trivalent metal ions ($Al^{3+}, Ga^{3+}, In^{3+}$) in aqueous solutions, the first solvation shells around metal ions are found to include six water molecules and display the hexacoordinate configuration [28]. Therefore, the first solvation shell of GlyZwitt.M$^{3+}$(H$_2$O)$_5$ complexes can be viewed as the solvation shell of M$^{3+}$(H$_2$O)$_6$ clusters with one water ligand substituted by Gly ligand. Actually, the strong electrostatic attraction between trivalent M$^{3+}$ ions and the negatively charged carboxyl group of Gly ligand provides a driving force for the reduction of the coordination number of M$^{3+}$ ions [29]. However, the computed results confirm the hexacoordinate configuration at the M$^{3+}$ ions for the first solvation shell of GlyZwitt.M$^{3+}$(H$_2$O)$_5$ complexes. During the sequential hydration of GlyZwitt.M$^{3+}$(H$_2$O)$_n$, $n = 0–5$, the electron delocalization from water molecules to the metal is found to weaken the electrostatic interaction between the metal ion and Gly ligand and give rise to the rotation of NH$_3^+$ group and the formation of intramolecular H bond in Gly ligand. Another finding is the appearance of intermolecular H bond between one water ligand and Gly ligand in GlyZwitt.M$^{3+}$(H$_2$O)$_6$ complexes ($n = 3–6$), which is associated with the polarization effect of M$^{3+}$ ions and the proton acceptor character of carboxyl oxygen of Gly ligand. This yields an energetically favorable pathway for the proton transfer from the inner shell to the outer shell, because the H–O bond length is enlarged for the water molecule with intermolecular H bond and the H$^+$ proton is likely to transfer to the outer shell.

2. Computational method

All the calculations were performed by GAUSSIAN 03 codes [30]. Geometrical optimization and spectra calculation for GlyZwitt.M$^{3+}$(H$_2$O)$_5$ complexes were conducted in the framework of density functional theory (DFT) through Becke’s three-parameter hybrid functional and Lee-Yang-Parr correlation functional (B3LYP) [31,32] with LanL2DZ basis sets [33,34]. The complex structures have been fully optimized with the convergence criteria for energy of 10$^{-6}$ hartree. The vibrational frequencies of the complexes were computed under harmonic approximation with the analytical force constants. The reliability and accuracy of B3LYP/LanL2DZ method were previously verified in the vibrational spectra calculation for a variety of the complexes formed by the metal and functional molecules [35–37]. The charge transfer between the metal and molecule is suggested to account for the enhancement of vibrational spectra [36,38].

The hydration reaction in the sequential microsolvation processes is defined as GlyZwitt.M$^{3+}$(H$_2$O)$_n$ + H$_2$O $\rightarrow$ GlyZwitt.M$^{3+}$(H$_2$O)$_{n+1}$, in which $n$ is the number of water molecule ligands binding to the metal ion. The solvation energy for the addition of the $n^\text{th}$ water molecule is calculated as the energy difference between GlyZwitt.M$^{3+}$(H$_2$O)$_{n+1}$ plus one free water molecule and GlyZwitt.M$^{3+}$(H$_2$O)$_n$ complex.

3. Results and discussion

To study the evolution of the geometry and the coordination of the microhydrated GlyZwitt.M$^{3+}$ complex as a function of the number $n$ of added water molecules, we performed the full structural optimizations on the individual complex, GlyZwitt.M$^{3+}$(H$_2$O)$_n$, $n = 1–6$. Figure 1 shows the optimized geometries of the GlyZwitt.M$^{3+}$(H$_2$O)$_n$ complexes. The Gly biomolecule is found to behave as a monodentate ligand in the complexes with the exception for GlyZwitt.In$^{3+}$(H$_2$O)$_2$ complex, which includes a bidentate Gly ligand. For $n = 1, 2$, the metal ion and monodentate ligands prefer a planar arrangement. A nonplanar tetrahedral geometry is obtained for the $n = 3$ complex. While the GlyZwitt.M$^{3+}$(H$_2$O)$_4$ complex exhibits the bipyramidal-trigonal geometry around the metal ions, the GlyZwitt.M$^{3+}$(H$_2$O)$_5$ complex shows a hexacoordinate configuration at the metal center. A spontaneous water migration to the outer solvation shell of the metal ions is found to occur during the optimization of the structures of initialized M$^{3+}$-hepta-coordinate GlyZwitt.M$^{3+}$(H$_2$O)$_5$ complexes, which leads to the M$^{3+}$ hexacoordination, as shown in Figure 1. Thus, the first solvation shell around the M$^{3+}$ metal ion consists of five water molecule ligands and one Gly bioligand with an octahedral arrangement around the metal center.

The coordination and reorganization of Gly and water molecule ligands surrounding M$^{3+}$ metal ion are strongly sensitive to the charge and ionic radius of the metal. The high charge of M$^{3+}$ ion yields the tight binding of ligands to the metal center, which provides a driving force for saturating the coordination shell of the metal ions [39]. On the other hand, a small ionic radius minimizes the space for positioning the ligands, resulting in a strong steric hindrance. The subtle equilibrium between the steric hindrance and the charge neutralization of the metal is expected to determine the stable coordination shell around the M$^{3+}$ metal ion.

In Figure 2 the bond lengths between M$^{3+}$ and carboxyl oxygen of Gly ligand in GlyZwitt.M$^{3+}$(H$_2$O)$_n$ complexes are plotted as a function of the number $n$ of water molecules. The bond length is found to increase with the increasing $n$, as a consequence of the charge transfer from the water molecule to the metal, which weakens the electrostatic interaction between the metal ion and Gly ligand. Figure 3 shows the distance between the carboxyl oxygen and amino hydrogen of Gly ligand varying as a function of $n$. The distance is reduced with the increasing $n$, and an intramolecular hydrogen bond is found to form with the rotation of NH$_3^+$ group in Gly ligand for GlyZwitt.M$^{3+}$(H$_2$O)$_5$ complex.

The rotation of NH$_3^+$ group and the disappearance of intramolecular hydrogen bond were reported previously for GlyZwitt.Cu$^{2+}$ complex as compared to GlyZwitt.Cu$^{+}$ complex [15], which is attributed to the electrostatic repulsion between the NH$_3^+$ group and Cu$^{2+}$ ion in addition to the weakness of the proton acceptor character of carboxyl oxygen upon ionization. In order to study the charge effect of M metal ions on the intramolecular hydrogen bond formation, we performed the structural optimizations of GlyZwitt.M$^{3+}$, GlyZwitt.M$^{2+}$ and GlyZwitt.M$^{+}$ complexes. It is found that the intramolecular hydrogen bond forms in GlyZwitt.M$^{3+}$ complexes (see Figure 4). Therefore, the appearance of intramolecular hydrogen bond in Gly ligand of GlyZwitt.M$^{3+}$(H$_2$O)$_5$ complex is associated with the reduced electrostatic interaction between the metal ion and Gly ligand, due to electron delocalization from water molecule to the metal. The Mulliken charge of the metal atoms in GlyZwitt.M$^{3+}$(H$_2$O)$_n$ complexes is collected in Table 1, which decreases with the stepwise addition of water molecule as a consequence of the charge transfer to the metal.

The intermolecular hydrogen bond is found to form between water molecule and Gly molecule in GlyZwitt.M$^{3+}$(H$_2$O)$_n$ complexes ($n = 3–5$). The hydrogen bond forms as well between the water molecule of the first solvation shell and water molecule of the second solvation shell in GlyZwitt.M$^{3+}$(H$_2$O)$_6$ complex. The H–O bond lengths of the water molecules associated with the formation of hydrogen bond are presented in Table 1. The formation of intermolecular hydrogen bonds is attributed to the polarization effect of the highly charged M$^{3+}$ ions on H–O bond of water molecules in the inner shell and the proton acceptor character of oxygen in Gly carboxyl or water molecule of the outer shell.
The hydration process is an exothermic process. The entropy for the inclusion of one water molecule yields a disfavoring factor for the hydration of GlyZwitt.M$^{3+}$ complexes. Due to the high charge of the metal, the large energy gain is obtained upon the addition of water molecule. The solvation energy is defined as the energy difference between GlyZwitt.M$^{3+}$(H$_2$O)$_n$ plus one free water molecule and GlyZwitt.M$^{3+}$(H$_2$O)$_n$ complex. The first water molecule provides the most noticeable 129.6 kcal/mol. A gradual decrease of the solvation free energies is found for the sequentially hydrated GlyZwitt.M$^{3+}$(H$_2$O)$_n$ complexes. This arises from the saturation of

![Figure 1. Optimized geometries of GlyZwitt.M$^{3+}$(H$_2$O)$_n$ complexes (M$^{3+}$ = Al$^{3+}$, Ga$^{3+}$, In$^{3+}$), n = 1–6.](image)

![Figure 2. Bond lengths (Å) between M$^{3+}$ and carboxyl oxygen of Gly ligand in GlyZwitt.M$^{3+}$(H$_2$O)$_n$ complexes as a function of the number n of water molecules. The squares denote the bond lengths of the complexes with M$^{3+}$ = Al$^{3+}$, circles indicate M$^{3+}$ = Ga$^{3+}$, and triangles indicate M$^{3+}$ = In$^{3+}$.](image)

![Figure 3. The distance (Å) between carboxyl oxygen and amino hydrogen of Gly ligand in GlyZwitt.M$^{3+}$(H$_2$O)$_n$ complexes as a function of the number n of water molecules. The squares denote the distances for the complexes with M$^{3+}$ = Al$^{3+}$, circles indicate M$^{3+}$ = Ga$^{3+}$, and triangles indicate M$^{3+}$ = In$^{3+}$.](image)
the coordination shell and the charge neutralization of the metal ion. The trend of the solvation energy for the sequential hydration is found as well in the DFT investigation of microsolvation of Al\textsuperscript{3+}-aromatic amino acid complexes\textsuperscript{[40]}. Table 1 collects the Mulliken charges of the metals and the solvation free energies.

Figure 5 presents the calculated infrared (IR) spectra of GlyZwitt.M\textsuperscript{3+}(H\textsubscript{2}O)\textsubscript{5} complexes. For GlyZwitt.Al\textsuperscript{3+}(H\textsubscript{2}O)\textsubscript{5} complex, an intense band appears at 2597.17 cm\textsuperscript{-1}. This band is assigned to the stretching mode of H–O bond of the water molecule ligand (with H bond) which forms the hydrogen bond with Gly molecule ligand. The intense bands at 847.80 and 838.87 cm\textsuperscript{-1} are associated with the rocking and wagging modes of the water molecules (without H bond) which do not form the hydrogen bond with Gly molecule. The strong band at 1543.57 cm\textsuperscript{-1} is due to the scissoring mode of the water molecule (with H bond) and the stretching mode of O–C bond of Gly molecule. The intense band at 3762.11 cm\textsuperscript{-1} is attributed to the asymmetric stretching mode of the water molecules (without H bond). The intense band at 783.48 cm\textsuperscript{-1} is associated with the rocking and wagging modes.

Table 1

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of the water molecules. The intense band at 1722.12 cm$^{-1}$ is associated with the scissoring mode of water molecules (without H bond). The intense band at 1140.21 cm$^{-1}$ is assigned to the wagging mode of the water molecule (with H bond). The strong band at 1010.77 cm$^{-1}$ is attributed to the wagging mode of the water molecule (with H bond) and the stretching mode of C–N bond of Gly molecule. The intense bands at 3760.48 and 3757.58 cm$^{-1}$ are assigned to the asymmetric stretching mode of the water molecules (without H bond). The intense band at 3663.52 cm$^{-1}$ is assigned to the symmetric stretching mode of the water molecules (without H bond). The vibrational frequencies and the band assignments for GlyZwitt.Ga$^{3+}$(H$_2$O)$_5$ and GlyZwitt.In$^{3+}$(H$_2$O)$_5$ complexes are almost the same as those of GlyZwitt.Al$^{3+}$(H$_2$O)$_5$ complex.

Figure 6 depicts the calculated Raman spectra of GlyZwitt.M$^{3+}$(H$_2$O)$_5$ complexes. For GlyZwitt.Al$^{3+}$(H$_2$O)$_5$ complex, most of the intense bands appear at the vibrational frequencies higher than 2500.00 cm$^{-1}$, which are associated with the stretching modes of H–O bonds of the water molecules, and H–C and H–N bonds of Gly molecule. The most intense band at 3667.95 cm$^{-1}$ is assigned to the symmetric stretching mode of H–O bonds of the water molecules (without H bond). The strong bands at 3761.63, 3760.48, 3753.68, 3757.58 and 3660.61 cm$^{-1}$ are also assigned to the symmetric and asymmetric stretching modes of H–O bonds of the water molecules (without H bond). The intense band at 3749.78 cm$^{-1}$ is associated with the stretching mode of short H–O bond of the water molecule (with H bond). The intense band at 2597.17 cm$^{-1}$ is attributed to the stretching mode of long H–O bond of the water molecule (with H bond). The intense bands at 3181.07 and 3114.27 cm$^{-1}$ display the symmetric and asymmetric stretching modes of H–C bonds of CH$_3$ group of Gly molecule. The strong bands at 3742.42 and 3283.21 cm$^{-1}$ are assigned to the symmetric and asymmetric stretching modes of H–N bonds of NH$_3$ group of Gly molecule. Other vibrational modes at lower frequencies are much weak and not discussed. The vibrational modes and the band assignments for GlyZwitt.Ga$^{3+}$(H$_2$O)$_5$ and GlyZwitt.In$^{3+}$(H$_2$O)$_5$ complexes are almost the same as those of GlyZwitt.Al$^{3+}$(H$_2$O)$_5$ complex.

The vibrational properties of GlyZwitt.M$^{3+}$(H$_2$O)$_5$ complexes predicted by the computed IR and Raman spectra can be verified by the experimental observation. The calculated IR spectroscopy of GlyZwitt.Al$^{3+}$(H$_2$O)$_5$ complex has the most intense band at 2597.17 cm$^{-1}$, which is associated with the stretching mode of H–O bond of the water molecule ligand forming the hydrogen bond with Gly molecule ligand. This vibrational mode can be used to identify the coordination and binding of Gly bioligand with Al$^{3+}$ cation in the microhydrated GlyZwitt.M$^{3+}$ gas phases. In a previous experimental study, IR spectra were measured for the mixtures of water and CD$_3$CN molecule with trivalent cations (Al$^{3+}$, Fe$^{3+}$, and Cr$^{3+}$) in the full concentration [41]. For the Al$^{3+}$:H$_2$O:CD$_3$CN solution, the frequency shift relative to the CN vibrational mode (2262 cm$^{-1}$) of CD$_3$CN molecule was used to identify the coordination and binding of CD$_3$CN molecule with Al$^{3+}$ cation. The largest shift (65 cm$^{-1}$) with respect to the CN peak of pure CD$_3$CN arises from the intermolecular interaction stronger than the interactions with water molecules, suggesting the direct binding of CD$_3$CN with Al$^{3+}$ cation. For the aqueous Ga(III) perchlorate and nitrate solutions, the measured Raman spectra demonstrated that the Ga(III) can exist as an inner-sphere complex, [Ga(OH)$_2$NO$_3$]$^{3+}$ [42]. During the future experimental measurement of IR spectra for the Al$^{3+}$:H$_2$O:Gly gas phases, the most intense band of the computed IR spectroscopy of GlyZwitt.Al$^{3+}$(H$_2$O)$_5$ complex at 2597.17 cm$^{-1}$ may be observed and identified as a useful characterization of the coordination and binding of Gly bioligand with Al$^{3+}$ cation. When the Al$^{3+}$:H$_2$O:Gly solutions are considered, the outer solvation shells must be included in the theoretical calculations for the microsolvation of GlyZwitt.M$^{3+}$ complexes in order to analyze the experimental results of the measured IR and Raman spectra. Surface Enhanced Raman Spectroscopy (SERS) can dramatically increase the sensitivity of Raman spectroscopy, which is a desirable method for identifying the binding events of amino acid residues [43,44]. Hence, SERS can be employed to study the interaction and binding of Gly ligand with the hydrated trivalent metal ions.

4. Conclusions

The equilibrium structures and energetic properties of GlyZwitt.M$^{3+}$(H$_2$O)$_n$ complexes (M$^{3+} = $ Al$^{3+}$, Ga$^{3+}$, In$^{3+}$), $n = 1–6$, were studied systematically with DFT method at B3LYP/LanL2DZ level. A first solvation shell is found with a hexacoordinate configuration at the metal center for GlyZwitt.M$^{3+}$(H$_2$O)$_5$, which arises from the delicate equilibrium between the steric hindrance and the charge transfer to the metal. The rotation of NH$_3$ group and the formation of intramolecular hydrogen bond in Gly ligand of the first solvation shell are associated with the electron delocalization from the water molecule to the metal, which leads to the weakness of the electrostatic interaction between the metal ions and Gly ligand. The vibrational modes of GlyZwitt.M$^{3+}$(H$_2$O)$_5$ complexes are characterized by the calculated IR and Raman spectra. Experiments are proposed to verify the predicted vibrational properties of the complexes.
Acknowledgments

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